Application of Linear, Nonlinear and Nanoscale Conductivity Spectroscopy for Characterising Ion Transport in Solid Electrolytes

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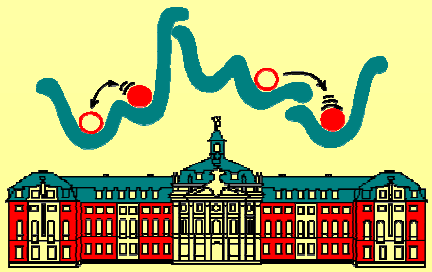
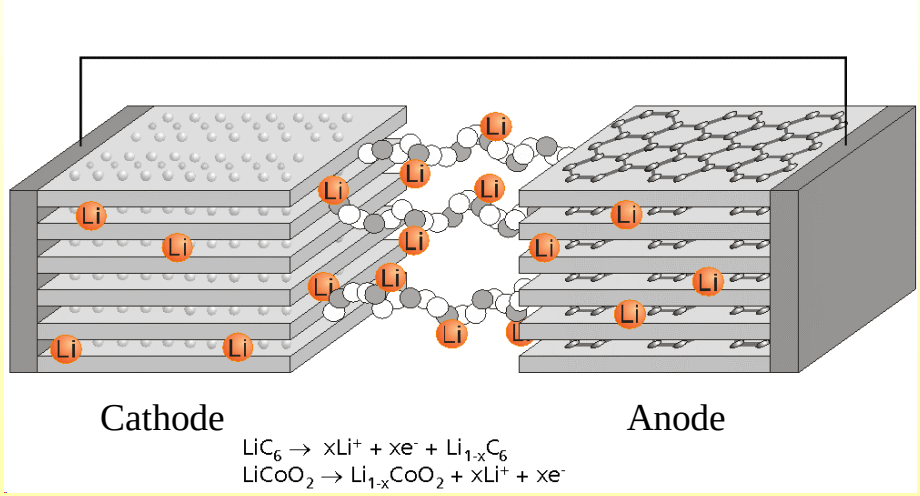


Fast ion conductors (superionic conductors):

Solid materials with conductivity > 10^{-3} S/cm at room temperature

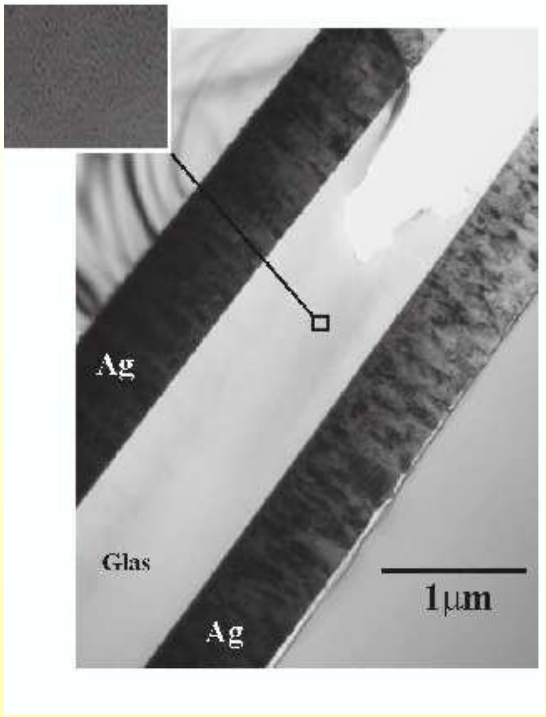
Areas of application:



Lithium batteries

Electrochromic windows

Thin films



F. Berkemeier, G. Schmitz,
University of Münster 2005

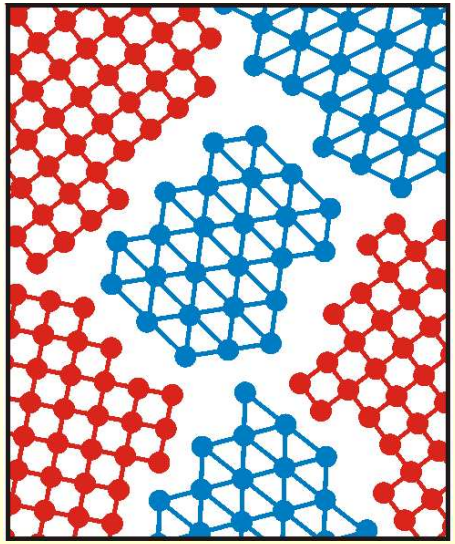
Preparation:
- RF magnetron sputtering
- Sol-gel methods and spin coating

Goals:
- Thickness of the order of 100 nm
- High chemical, electrochemical and mechanical stability
- Conductivity: 10^{-5} – 10^{-4} S/cm

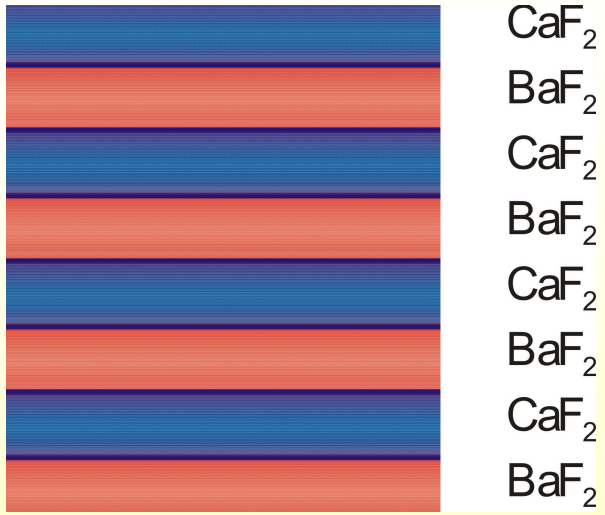
High electric fields: 5 V / 100 nm = 500 kV/cm !

⟶ Field-dependent ionic conductivity

Nano- and mesostructured ionic conductors



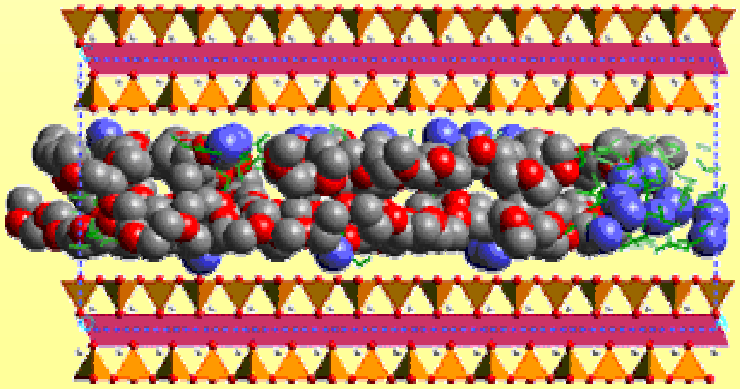
P. Heitjans, S. Indris,
Phys. Cond. Mat.
15 (2003) R1257.



N. Sata et al.
Nature **408**
(2000) 946

Conductor-Insulator
nanocomposites

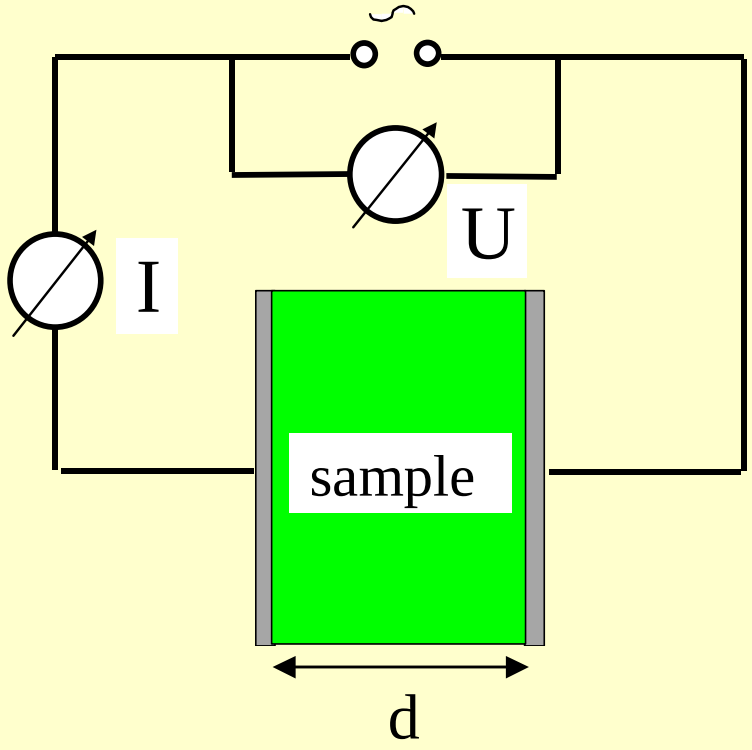
Heterolayered
conductors



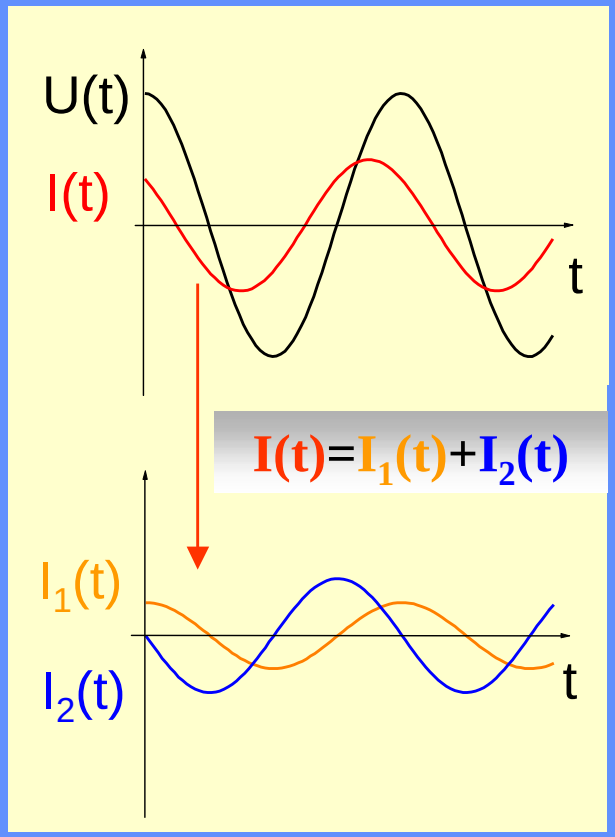
Nanogel electrolytes

M. M. E. Jacob et al.,
J. Mat. Chem. **13** (2004) 1.

1. Linear Conductivity Spectroscopy



A = contact area between sample and electrodes



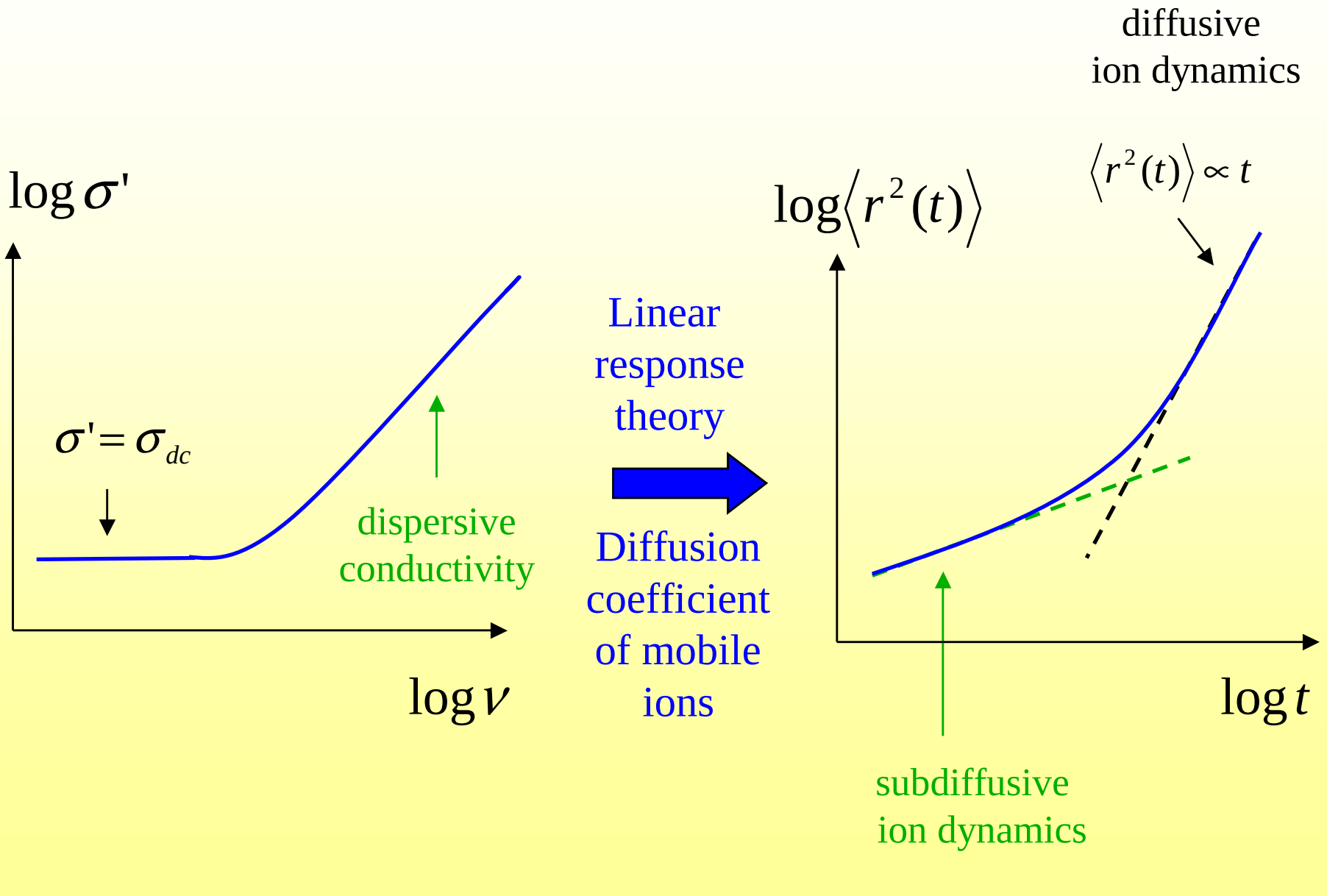
$$\sigma'(\omega) = (I_{0,1}/U_0) * (d/A)$$

Measure for dissipated electrical energy

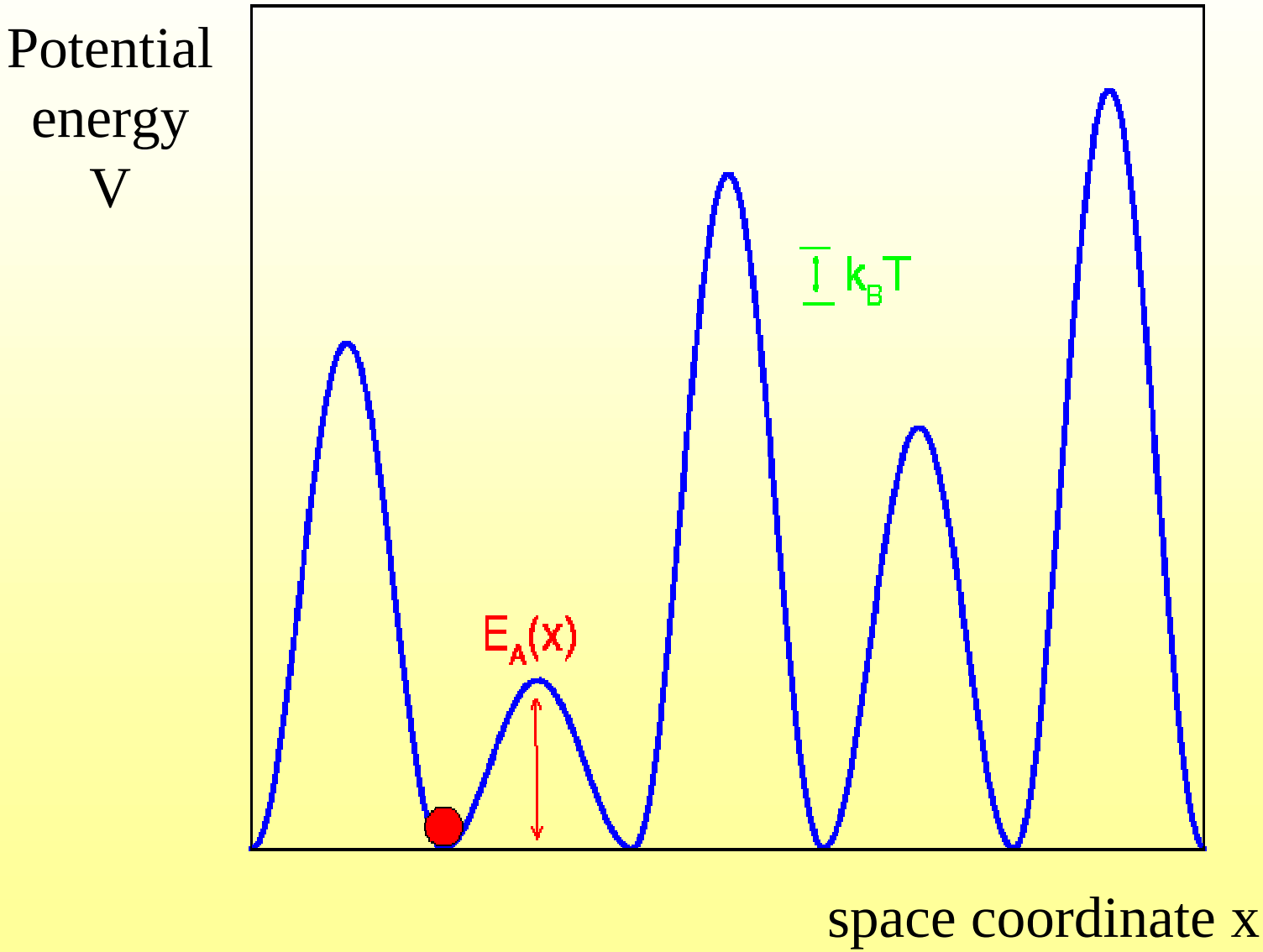
$$\sigma''(\omega) = (I_{0,2}/U_0) * (d/A)$$

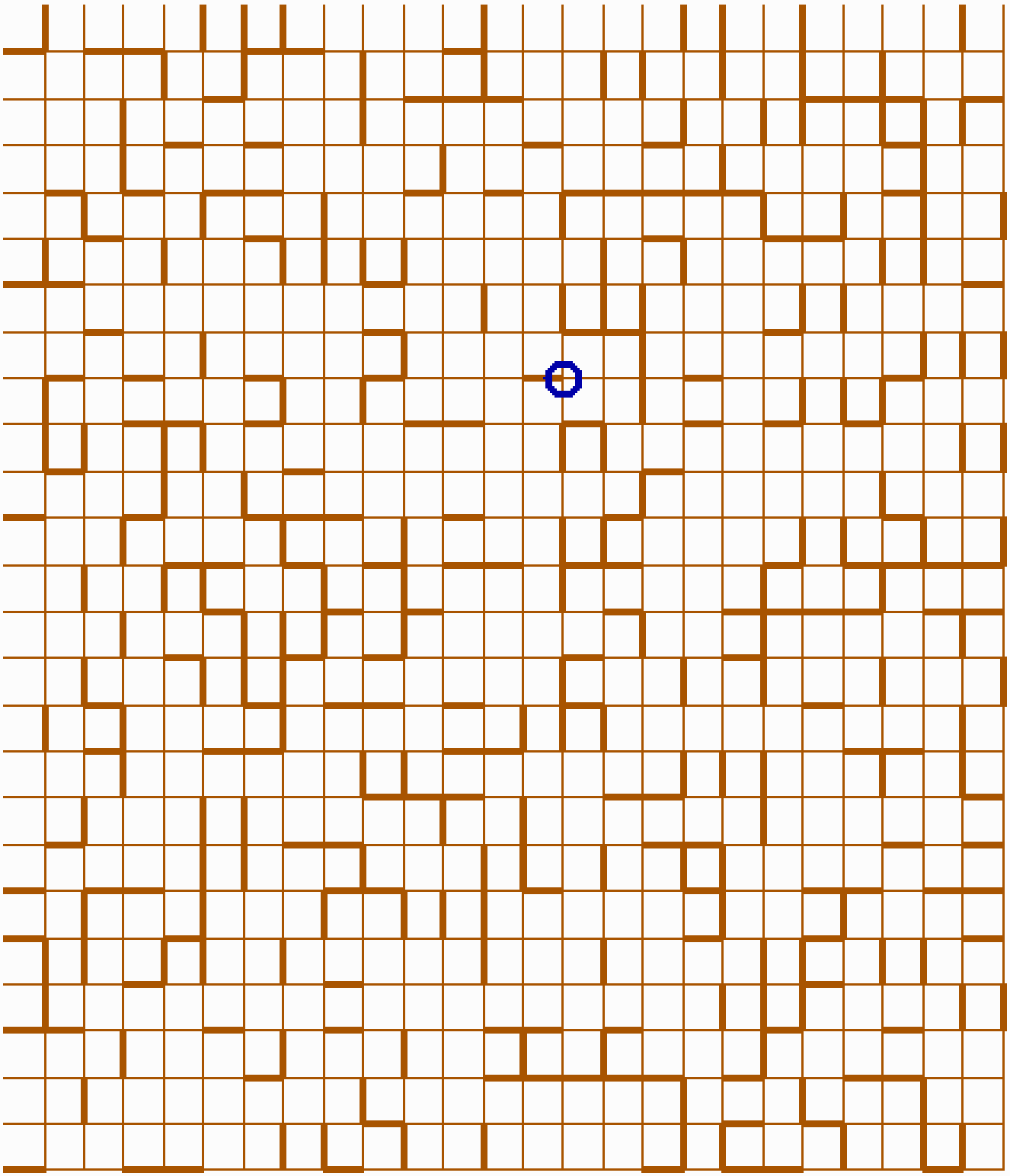
Measure for stored electrical energy

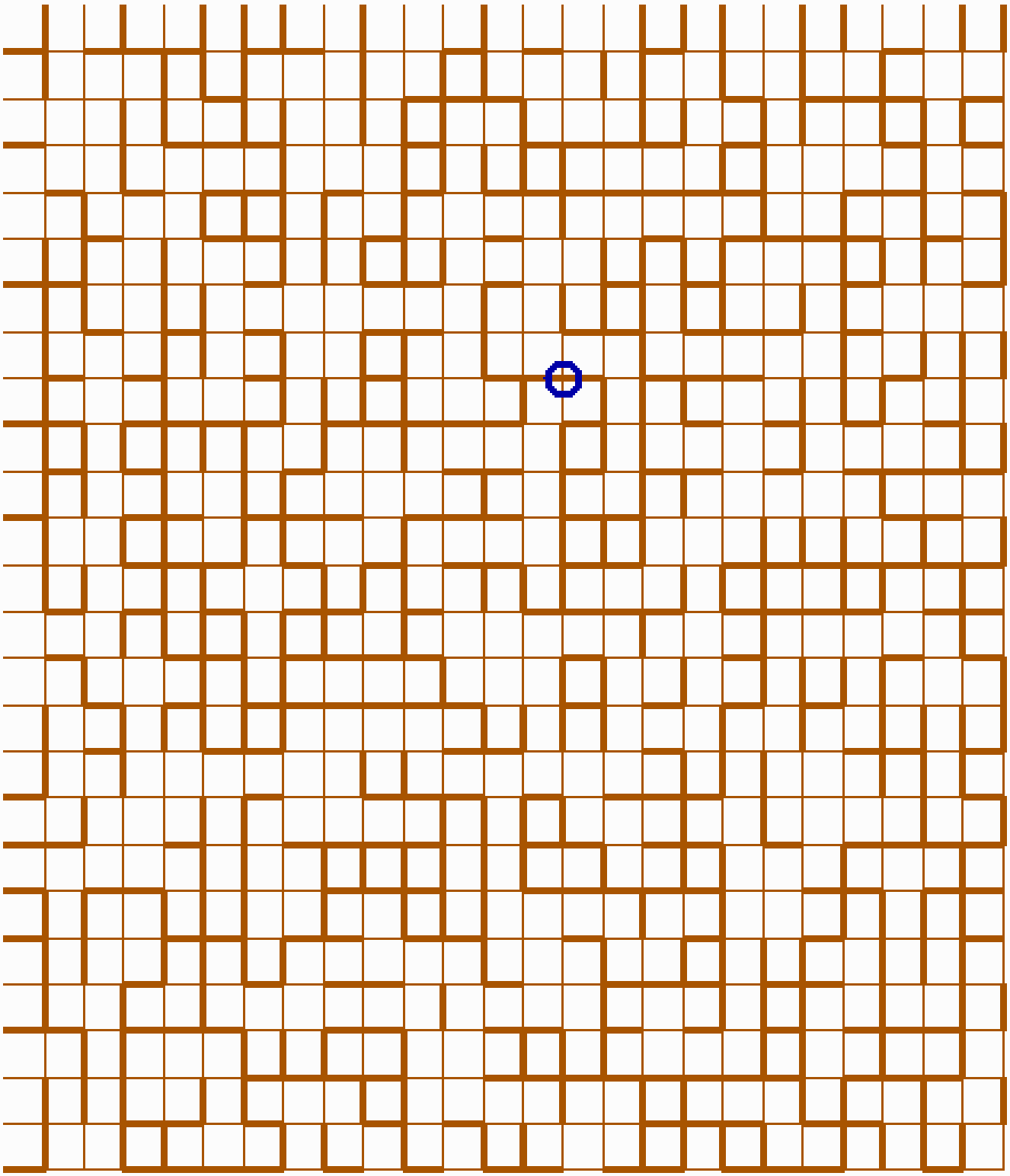
Linear response theory



Random barrier model







Spectra of Ion Conducting Glasses

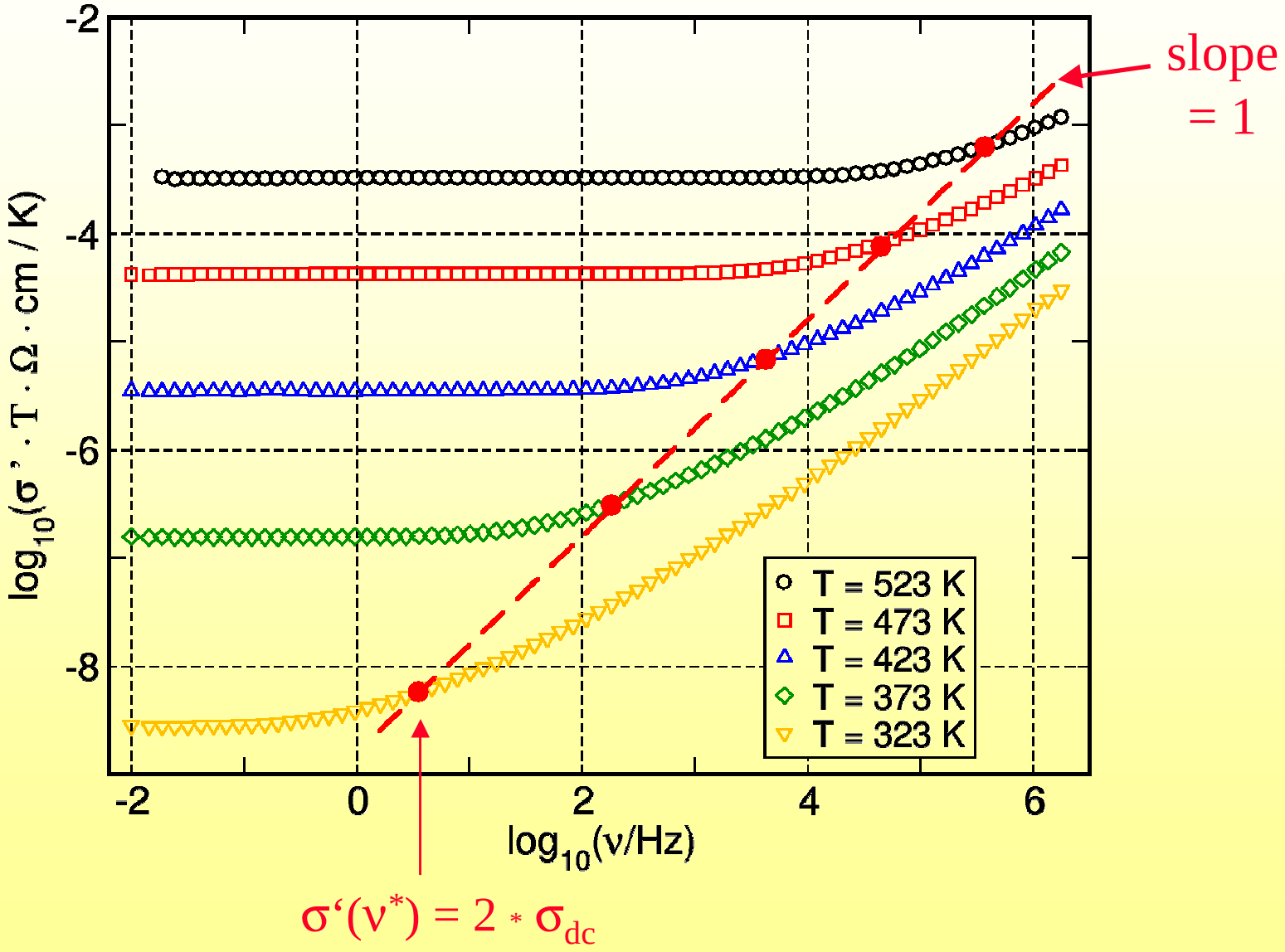
Variation of compositional parameters:

- Number density of mobile ions
- Structure of glass network (solid matrix)

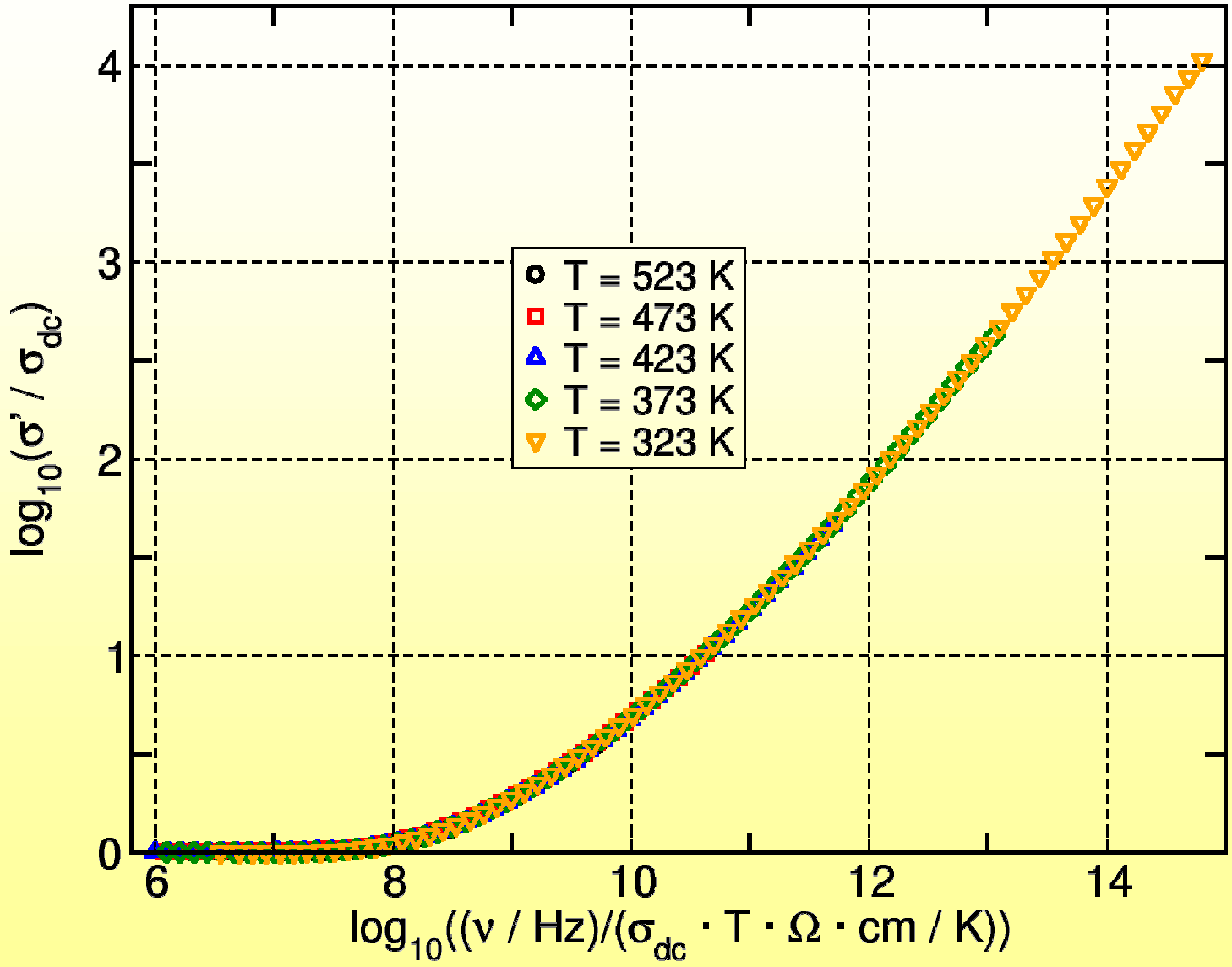
Quasi-universal shape of conductivity spectra
(virtually independent of composition)

Is there a quasi-universal ion transport mechanism?

Conductivity spectra of a 0.213 Na_2O * 0.787 GeO_2 glass

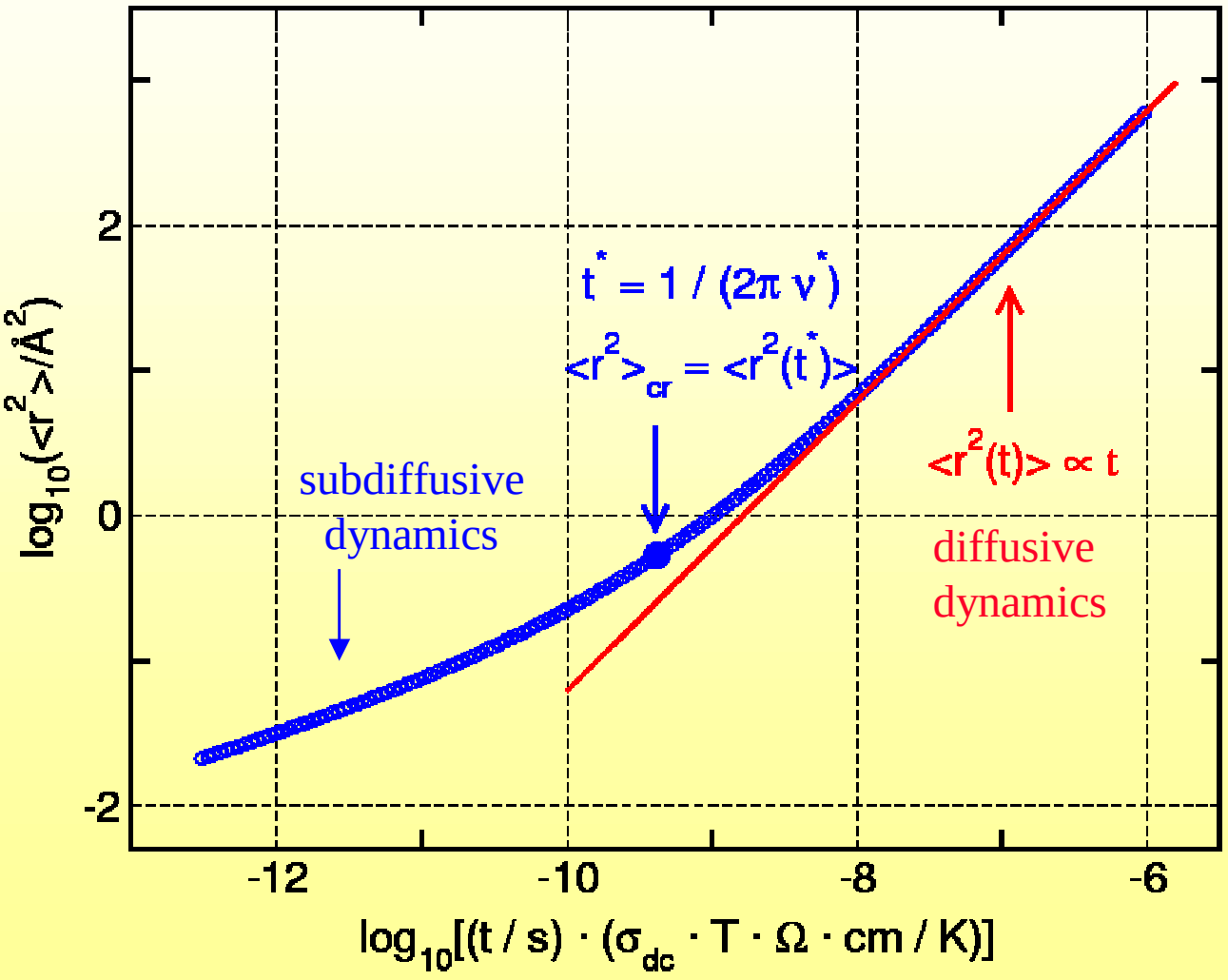


Summerfield scaling

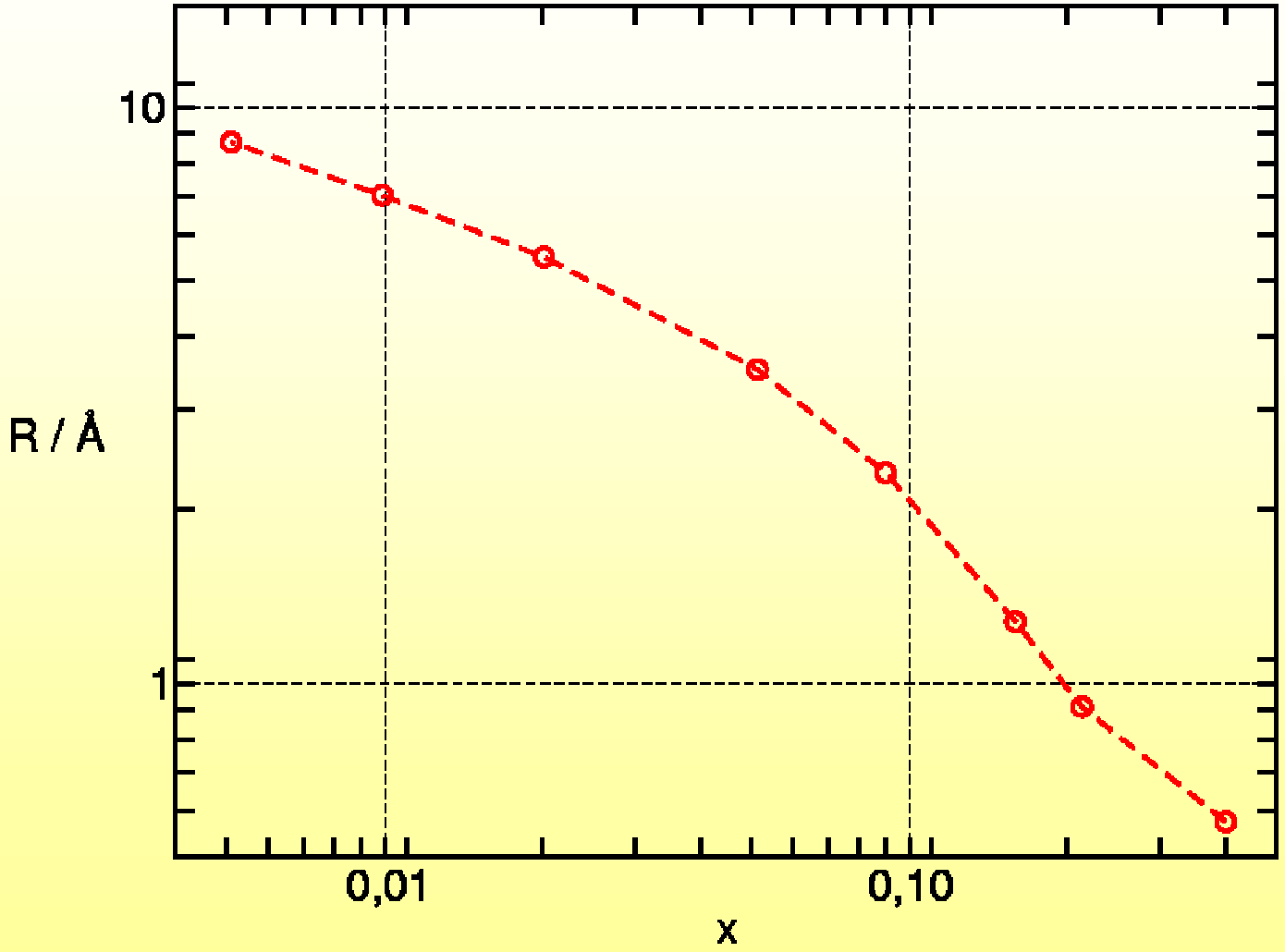


Master curve of the time-dependent mean square displacement of the mobile Na^+ ions, $<r^2(t)>$

0.213 Na_2O * 0.787 GeO_2 glass



Spatial extent of subdiffusive ion dynamics R $\equiv \sqrt{\langle r^2 \rangle_{cr}}$
for x Na_2O * (1 - x) GeO_2 glasses



B. Roling, C. Martiny, S. Brückner, *Phys. Rev. B* **63** (2001) 214203.

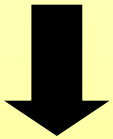
Assumption: Typical hopping distance of Na^+ ions: $d \approx 3\ \overset{o}{A}$
(Molecular dynamics simulations)

Glass with x = 0.005: $\langle r^2 \rangle_{cr} > d^2$

→ At the crossover time t^*, the ions have moved, on the average, over *several hopping distances*.

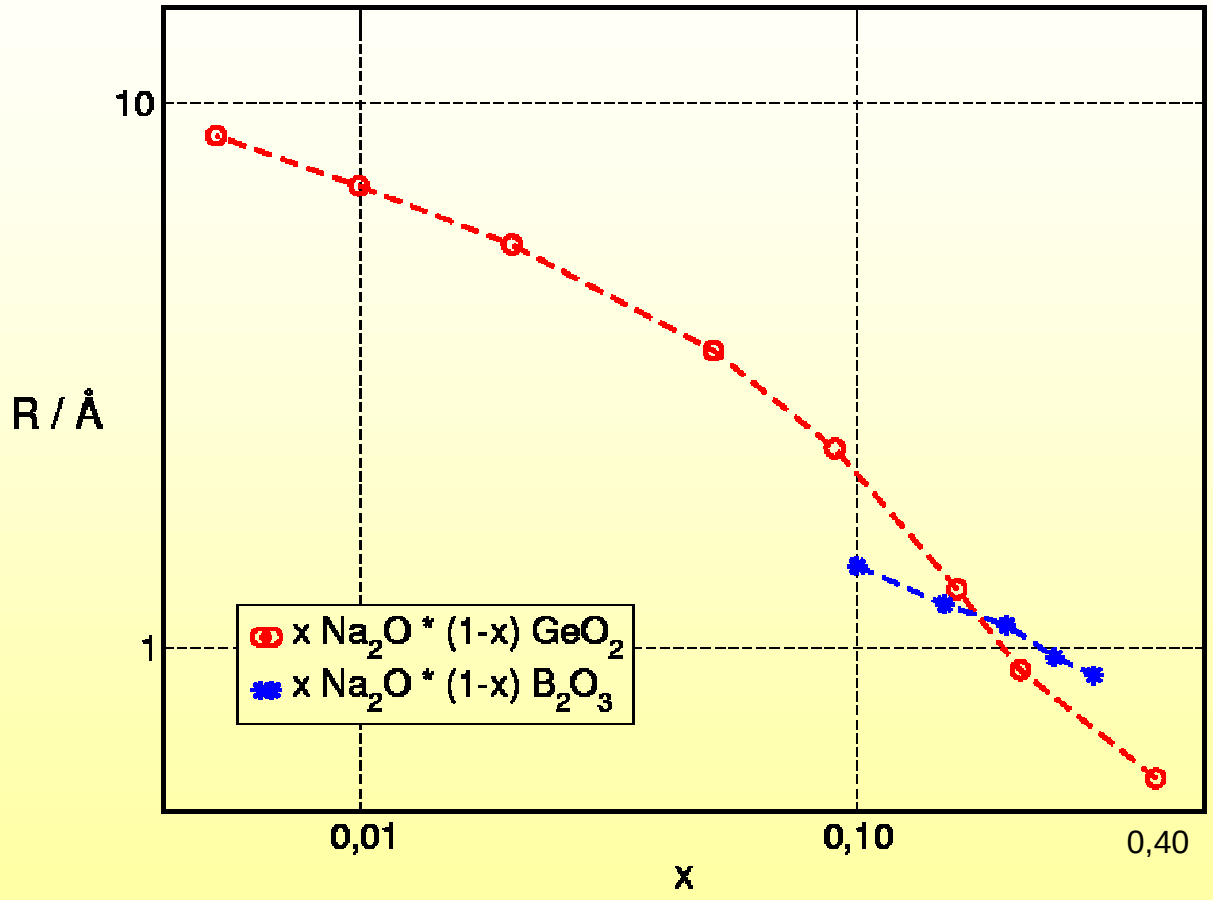
Glass with x = 0.40: $\langle r^2 \rangle_{cr} < d^2$

→ At the crossover time t^*, only a *small fraction of ions* have left their original sites.



Despite the quasi-universal shape of the conductivity spectra, the microscopic mechanisms of the ion transport depend on glass composition.

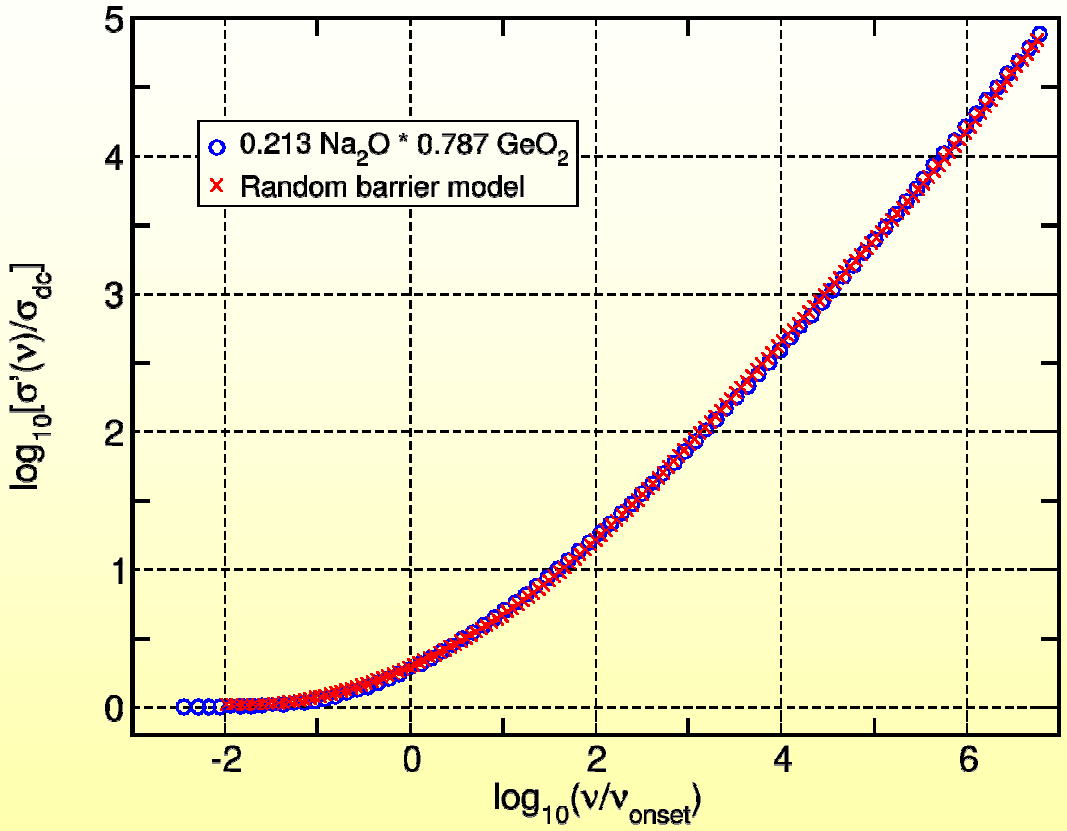
Spatial extent of subdiffusive ion dynamics R
for x Na_2O * (1 - x) GeO_2 and x Na_2O * (1 - x) B_2O_3 glasses



B. Roling, C. Martiny, S. Brückner, *Phys. Rev. B* **63** (2001) 214203.

⟶ R depends on *structure of the glass network.*

Comparison with Random Barrier Model



B. Roling,
Phys. Chem. Chem. Phys.
3 (2001) 5093.

See also:
J. C. Dyre, T. Schroeder,
Rev. Mod. Phys.
72 (2000) 873.

However: Random Barrier Model: $\left\langle r^2 \right\rangle_{cr} \propto T^{-1.3}$ (Number of continuous conduction pathways depends on temperature.)

Most ion conducting glasses: $\left\langle r^2 \right\rangle_{cr}$ independent of T

Almond and West formalism

- Determine crossover frequency ν^*
- Take random walk expression: $\sigma_{dc} = \frac{N_{V,\text{mobile ions}} \cdot q^2 \cdot a^2 \cdot \Gamma}{6 \cdot k_b \cdot T}$

  and identify crossover frequency ν^* with hopping rate Γ
- Assumption for hopping distance: $a = 2.5 - 3\ \text{Å}$

→ Number density of mobile ions $N_{V,\text{mobile ions}}$

Problem: Random walk expression is not valid!

In a first approximation: $\frac{N_{V,\text{mobile ions}}}{N_{V,\text{all ions}}} \approx \frac{\langle r^2 \rangle_{cr}}{a^2}$

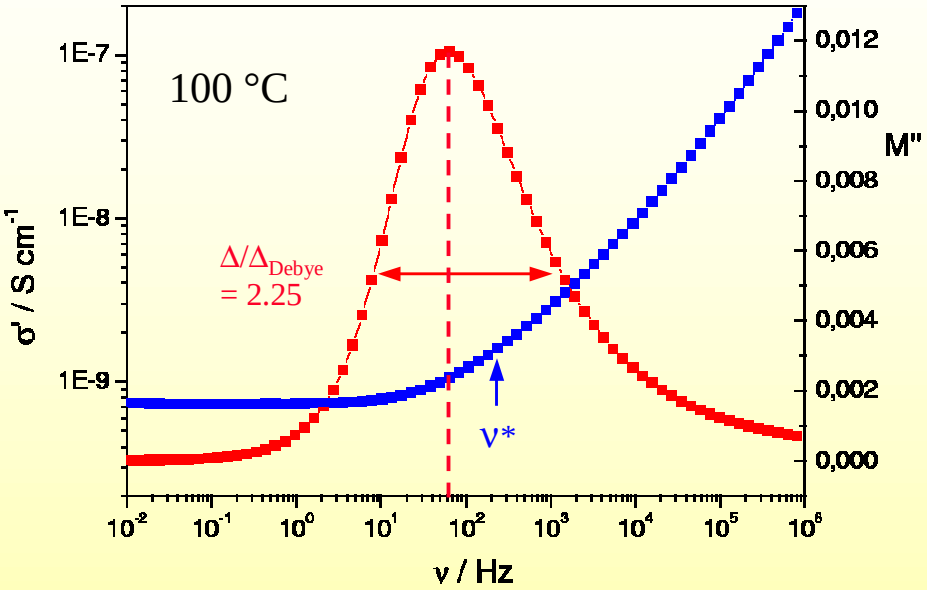
→ Number of ions that have moved at the crossover time t^*

(**Not** number of ions that contribute to dc conductivity!)

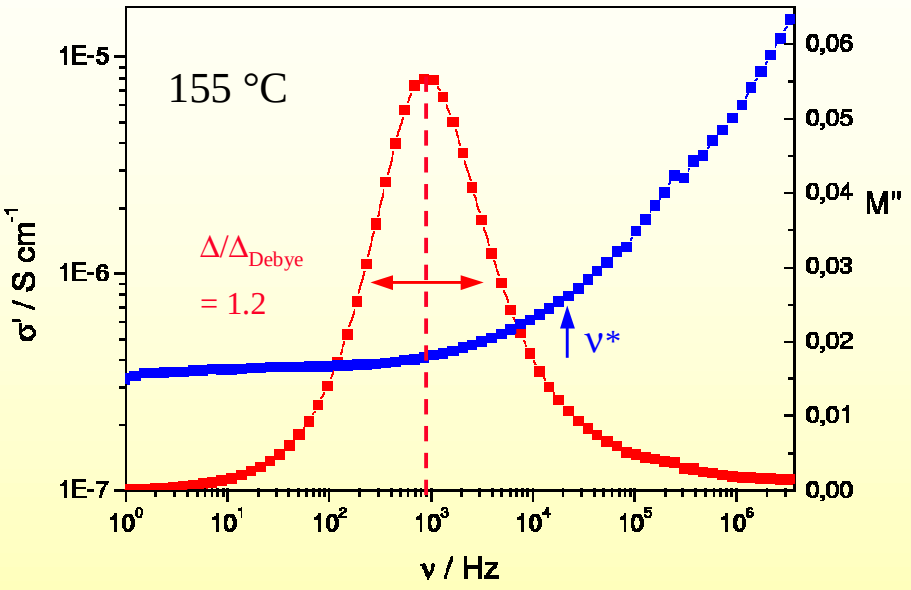
Modulus formalism

$$\hat{M} = \frac{1}{\hat{\varepsilon}} = \frac{i \cdot \omega \cdot \varepsilon_0}{\hat{\sigma}}$$

0.20 Na_2O * 0.80 GeO_2



0.0005 K_2S * 0.9995 B_2S_3



$$\frac{\nu_{M'' \ peak}}{\nu^*} \approx \frac{\Delta\varepsilon}{\varepsilon'(\infty)}$$

Dielectric relaxation strength due to subdiffusive ion dynamics

Vibrational and electronic polarisation

With decreasing mobile ion concentration, Δε decreases and the modulus peak shifts into the dc conductivity regime.

Misinterpretation of modulus peak narrowing with decreasing ion concentration:

With decreasing ion concentration, the ionic movements become less correlated.

Correct interpretation of conductivity spectra using linear response theory:

With decreasing ion concentration, the spatial extent of the subdiffusive ion dynamics (of the correlated forward-backward movements) increases!

2. Nonlinear (High-Field) Conductivity Spectroscopy

Example: Solid electrolyte sample with thickness d = 100 nm

Applied voltage U = 5 V

⟶ Electric field strength E = 500 kV / cm

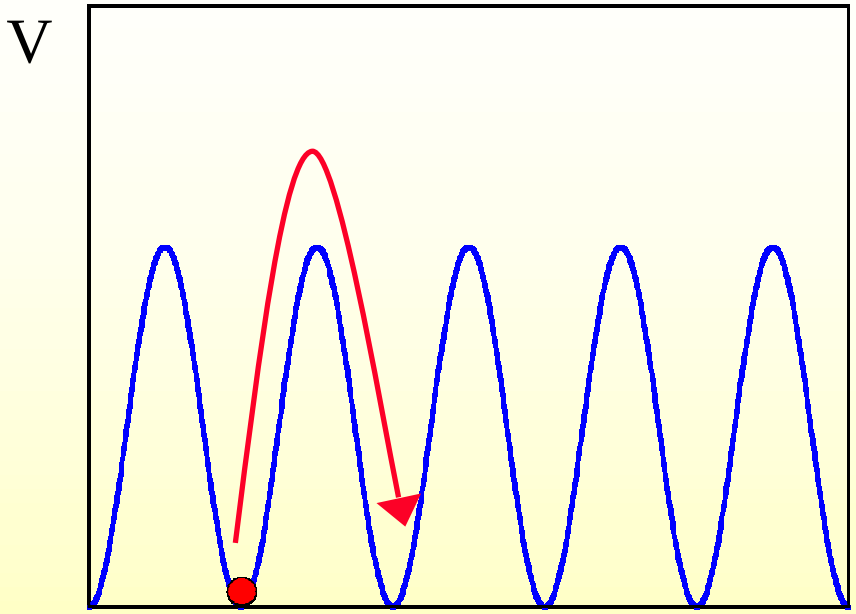
At field strengths E > 50 kV/cm, the ionic conductivity of many solid electrolytes becomes field-dependent.

Current density $j = \sigma_1 \cdot E + \sigma_3 \cdot E^3 + \sigma_5 \cdot E^5 + ...$

Low-field conductivity

Higher-order conductivity coefficients

‘Random walk‘ in a periodic potential landscape



Current density

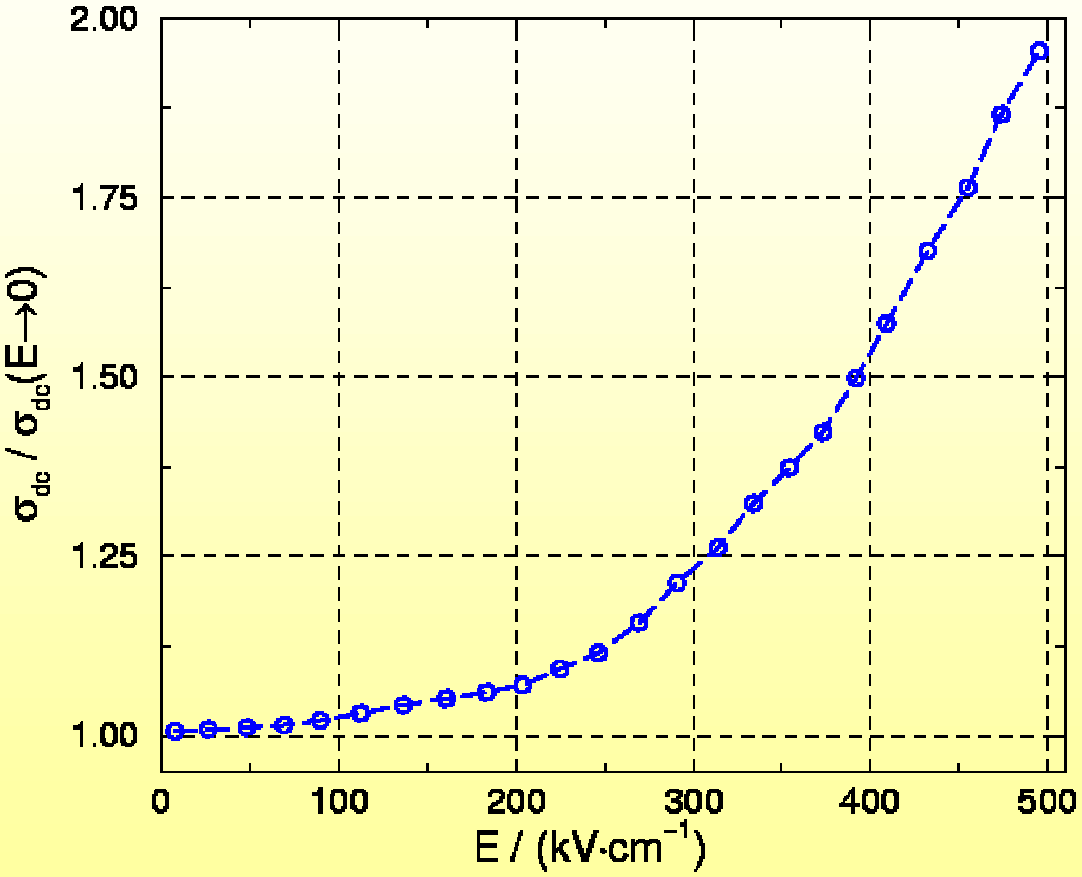
$$j \propto \sinh\left(\frac{qaE}{2kT}\right)$$

q = charge of particle
k = Boltzmann‘s constant
T = temperature

Field dependence of current density provides *direct information* about jump distance a.

Field dependence of the dc conductivity of solid electrolytes

Thuringian glass: 0.101 Na_2O * 0.084 CaO * 0.030 Al_2O_3 * 0.785 SiO_2



Fit with

$$j \propto \sinh\left(\frac{qa_{app}E}{2kT}\right)$$

Apparent jump distance

a_{app} = 15 Å ... 30 Å

(found for various glasses)

J. M. Hyde et al., Phys. Chem. Glasses 27 (1986) 147.

Previous studies: DC electric fields

- No direct information on Joule heating
  (Joule heating may pretend nonlinear ion transport.)

- Only one relation: $\sigma_{dc}(E_{dc})$

Our method: AC electric fields

- Unambiguous differentiation between nonlinear ion transport and Joule heating

- $\sigma_1(\nu)$, $\sigma_3(\nu)$, $\sigma_5(\nu)$, ...

  ➡ More information

Glasses studied:

- 0.127 Na_2O * 0.096 CaO * 0.062 Al_2O_3 * 0.715 SiO_2 (NCAS12)

[Composition similar to Thuringian glass: a_{app} = 15.5 Å (from sinh fit)]

- 0.25 Na_2O * 0.096 CaO * 0.062 Al_2O_3 * 0.592 SiO_2 (NCAS25)

- 0.20 Na_2O * 0.80 SiO_2

- 0.25 Na_2O * 0.75 SiO_2

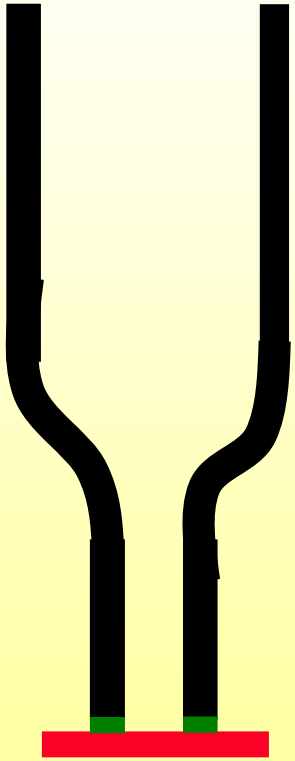
Preparation of thin glass samples

- High-precision cutting and grinding of bulk glass samples:

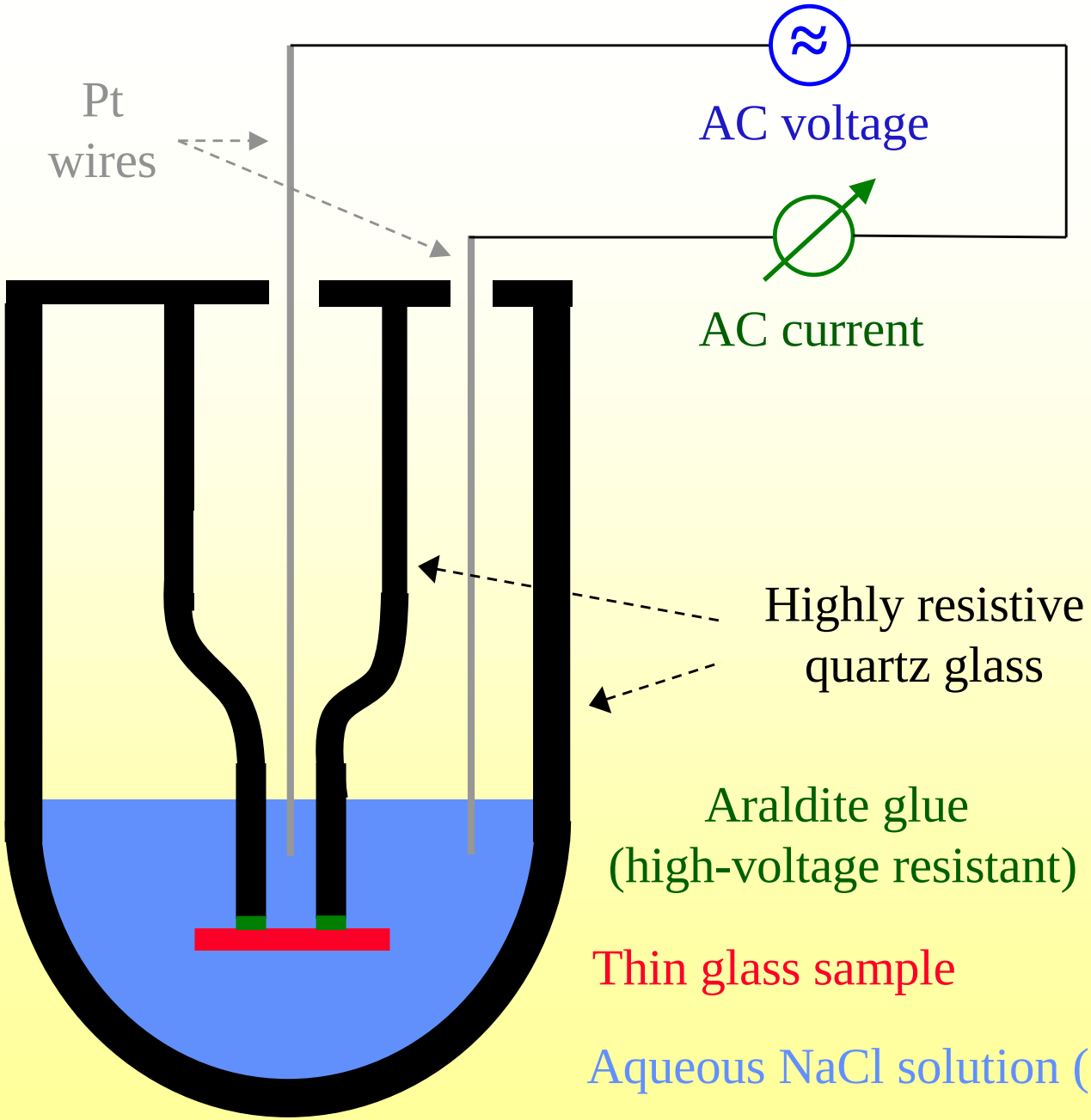
  ⟶ Sample thickness: 60 – 100 μm

- Samples are attached to high-resistance quartz glass tube ($\sigma < 10^{-16}$ S/cm) by using a high-voltage resistant araldite glue.

- Chemical etching with HF: 40 - 50 μm



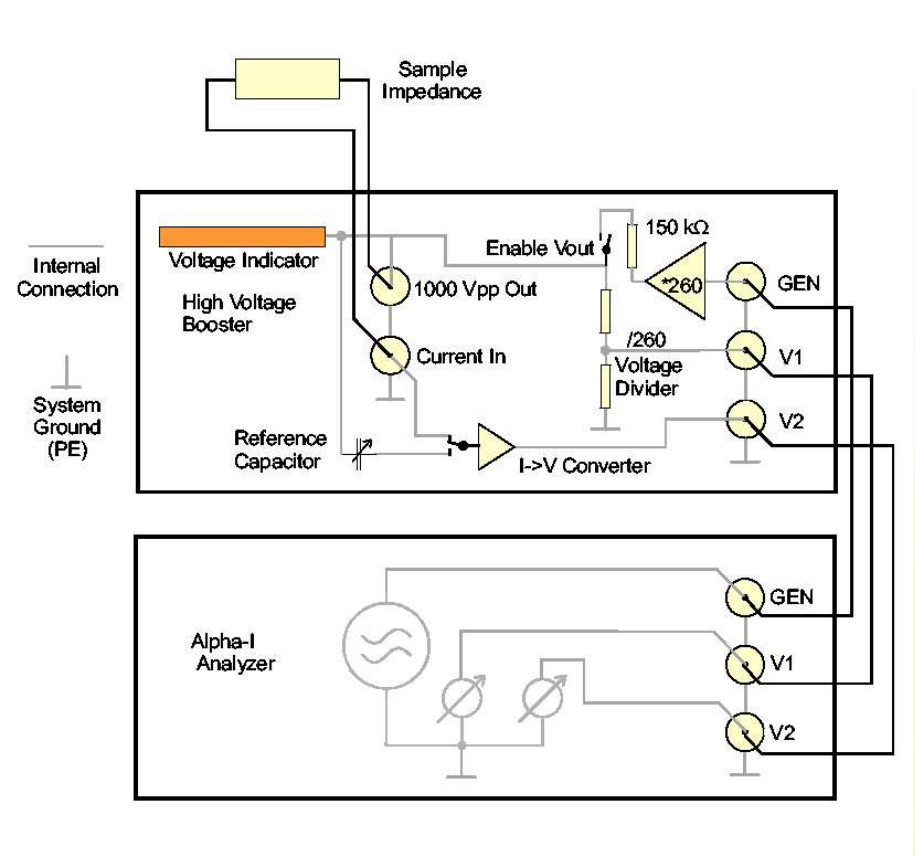
➡ Electric fields of 100 - 125 kV /cm at U = 500 V


Pt
wires
AC voltage
AC current
Highly resistive
quartz glass
Araldite glue
(high-voltage resistant)
Thin glass sample
Aqueous NaCl solution (1 mol/l)

High-voltage measurement system

Novocontrol α-S High Resolution Dielectric Analyser, equipped with:

- Broadband High-Voltage Amplifier,
- Broadband Dielectric Converter



Frequency range: < 10 kHz

Maximum amplitude of
ac voltage: 500 V

Detection of **higher harmonics** in current spectra

Analysis of nonlinear ion transport by means of higher harmonics

Example: Electrical properties of ion conducting sample are given by:

$$j = \sigma_1 \cdot E + \sigma_3 \cdot E^3$$

Electric field $E = E_0 \cdot \sin(\omega t)$

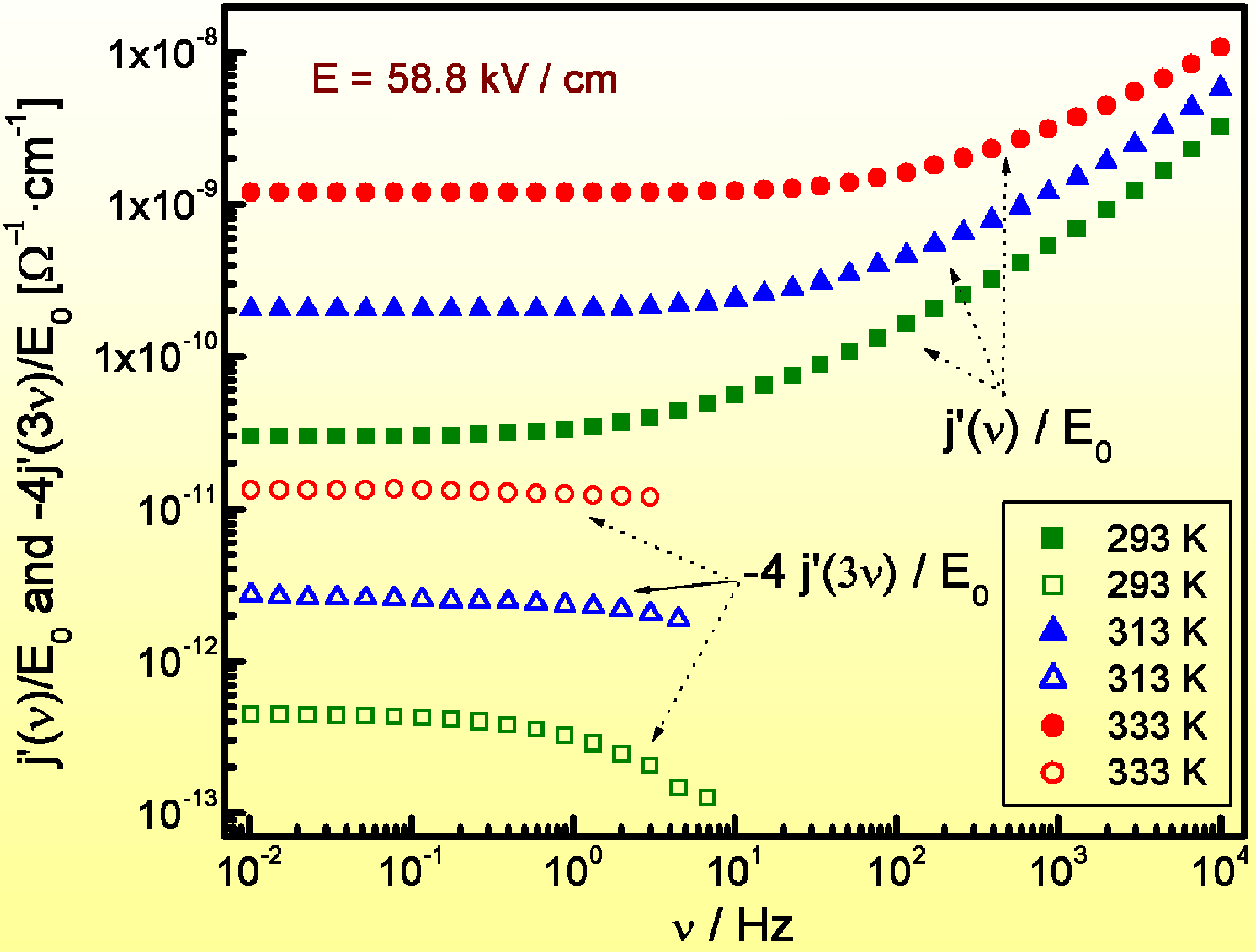
$$j = \sigma_1 \cdot E_0 \cdot \sin(\omega t) + \sigma_3 \cdot (E_0)^3 \cdot \sin^3(\omega t)$$

$$= \sigma_1(\omega) \cdot E_0 \cdot \sin(\omega t) + \frac{3}{4}\sigma_3(\omega) \cdot (E_0)^3 \cdot \sin(\omega t) \underbrace{- \frac{1}{4}\sigma_3(3\omega) \cdot (E_0)^3 \cdot \sin(3\omega t)}$$

Harmonic at 3ω

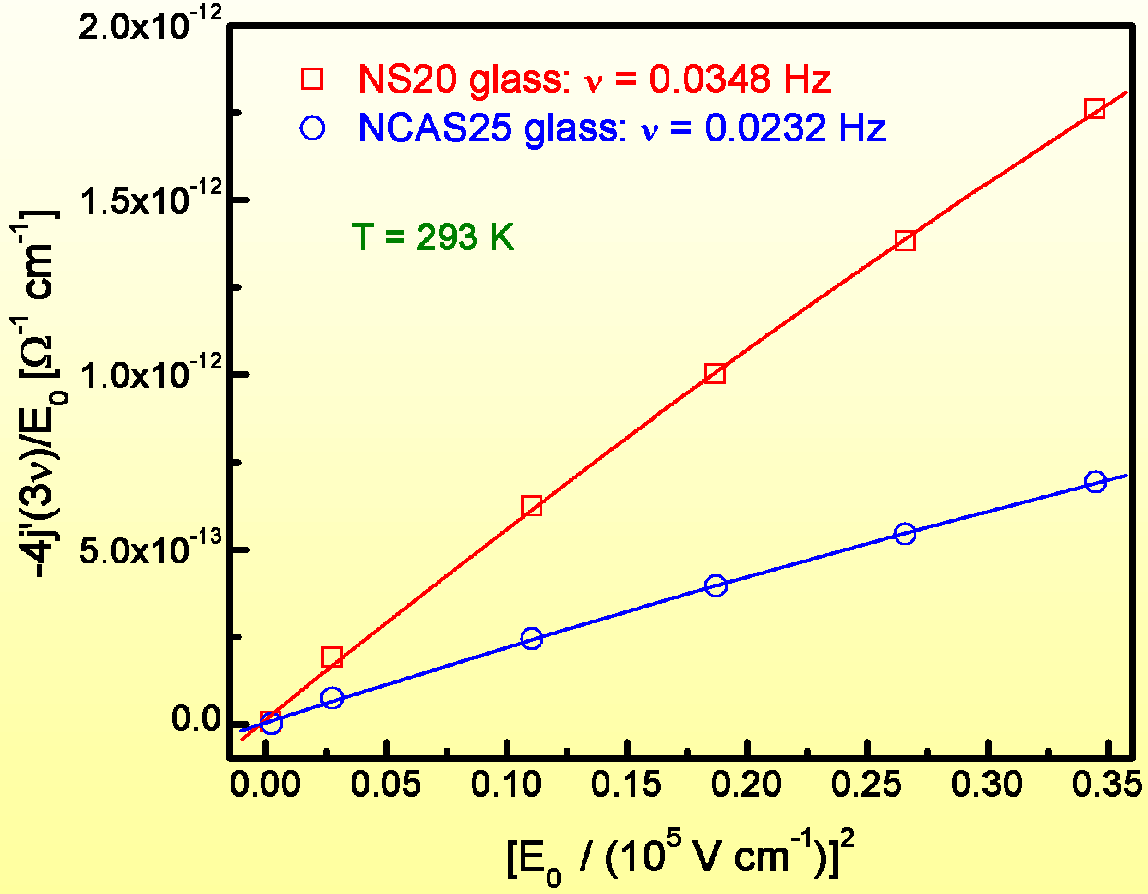
Unambiguous differentiation between nonlinear ion transport and Joule heating.

Results for 0.2 Na_2O * 0.8 SiO_2 glass (NS20)



Determination of higher-order conductivity coefficients

$$\frac{-4\cdot j'(3\nu)}{E_0} = \sigma_3'(3\nu)\cdot(E_0)^2 + \frac{5}{4}\cdot\sigma_5'(3\nu)\cdot(E_0)^4 + ...$$



Fit by second-order polynomial

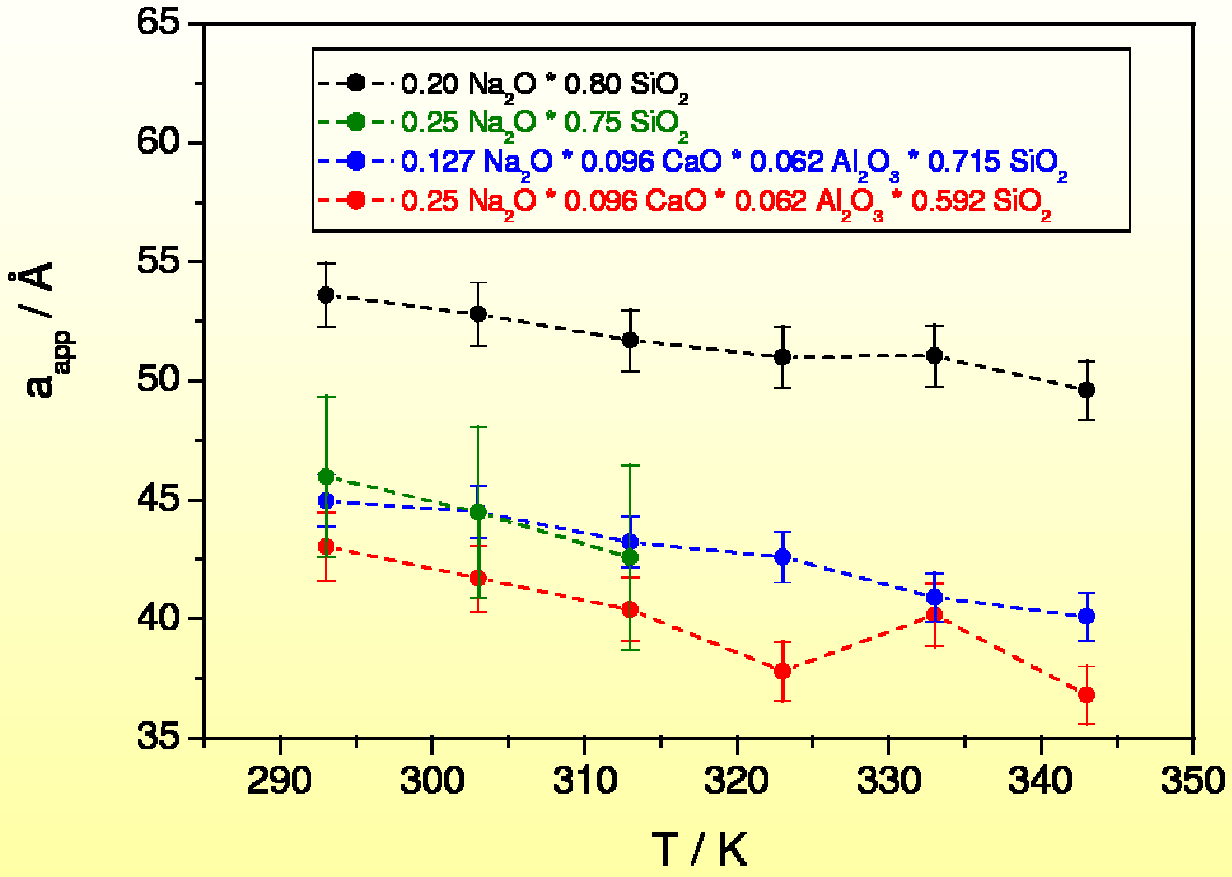
→ Linear term: $\sigma_{3,dc}$

→ Negative quadratic term: $\sigma_{5,dc} < 0$

Apparent jump distances

$$a_{app} = \sqrt{\frac{\sigma_{3,dc} \cdot 24 \cdot (kT)^2}{\sigma_{1,dc} \cdot q^2}}$$

(Taylor expansion of sinh function)



Taylor expansion of sinh function:

$\sigma_{5,dc} > 0$

↕

Experiment:

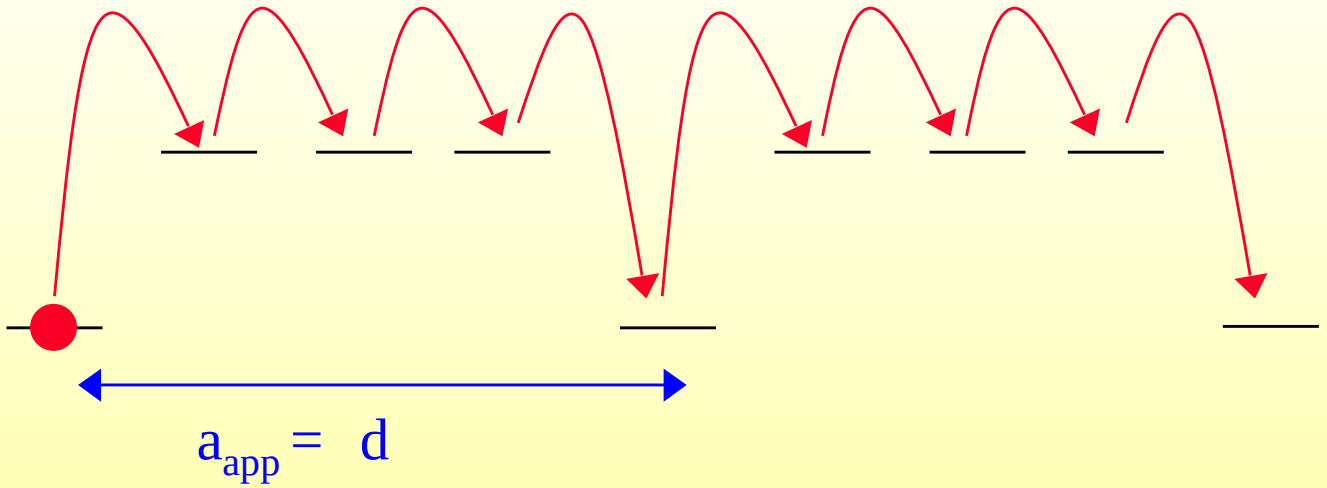
$\sigma_{5,dc} < 0$

- Values are larger than literature values from dc measurements.
- a_{app} decreases with increasing temperature T.
- a_{app} decreases with increasing Na_2O content.

What is the physical meaning of the apparent jump distance?

(Collaboration with Prof. Andreas Heuer, Insitute of Physical Chemistry, and Prof. Rudolf Friedrich, Institute of Theoretical Physics, Münster)

One-dimensional periodic potential landscape:



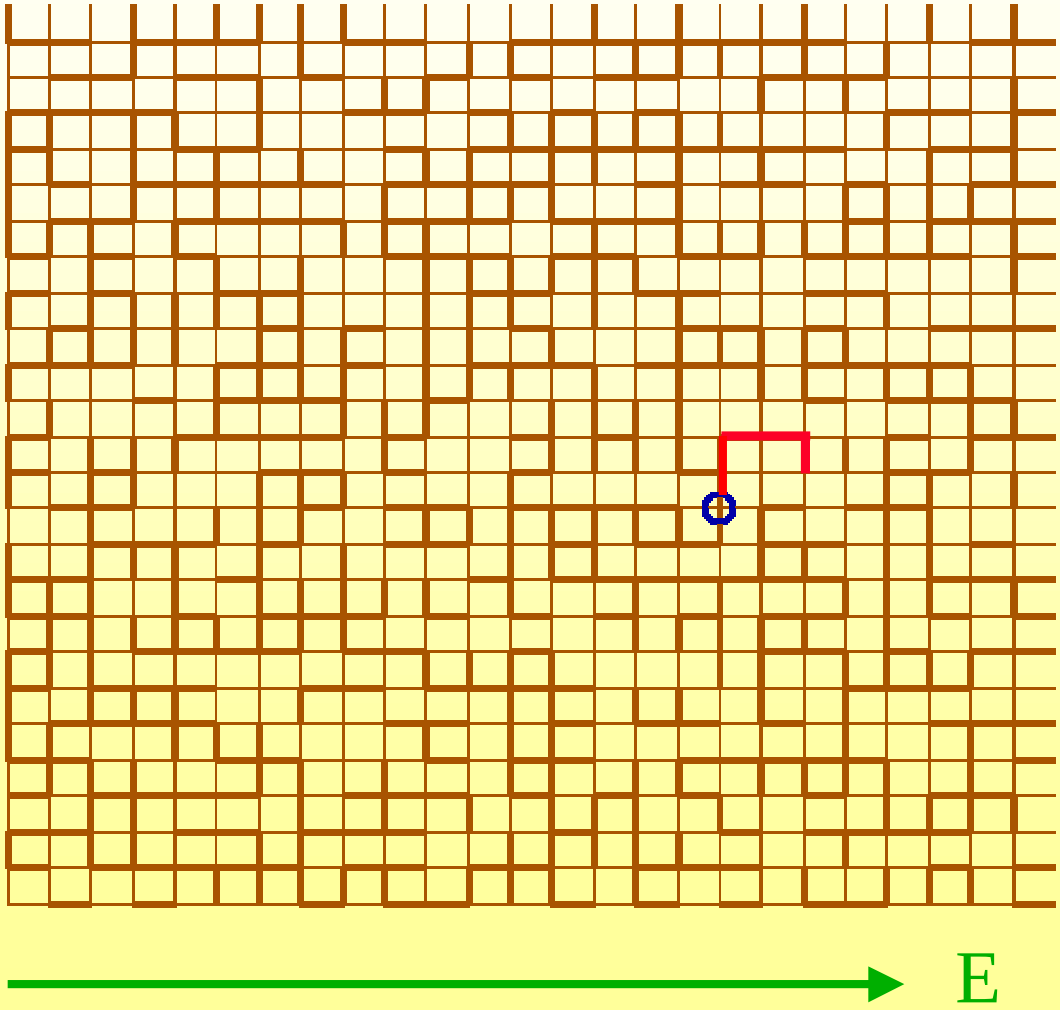
→ Is the apparent jump distance related to the distance between **low-energy sites** in an ionic conductor?

However: Things become more complicated in **two- and three-dimensional disordered potential landscapes.**

Nonlinear conductivity of particles in a random barrier landscape

Monte Carlo simulations: $\sigma_{3,dc}$ is negative!

B. Roling, *J. Chem. Phys.* **117** (2002) 1320.



Field-induced trapping of particles in dead ends

Summary and Outlook

- Apparent jump distance a_{app} decreases with increasing temperature and increasing sodium oxide content.

- The fifth-order coefficient $\sigma_{5,dc}$ is negative (for all glasses and at all temperatures).

- Random Barrier Model predicts negative values for $\sigma_{3,dc}$. Experimental values for $\sigma_{3,dc}$ are positive.

- Further theoretical studies on nonlinear ion transport in disordered potential landscapes

→ Deeper understanding of physical meaning of large apparent jump distances and of negative values for $\sigma_{5,dc}$

3. Electrostatic force spectroscopy (Nanoscale conductivity spectroscopy)

Established methods for characterising ion dynamics and transport in solid electrolytes:

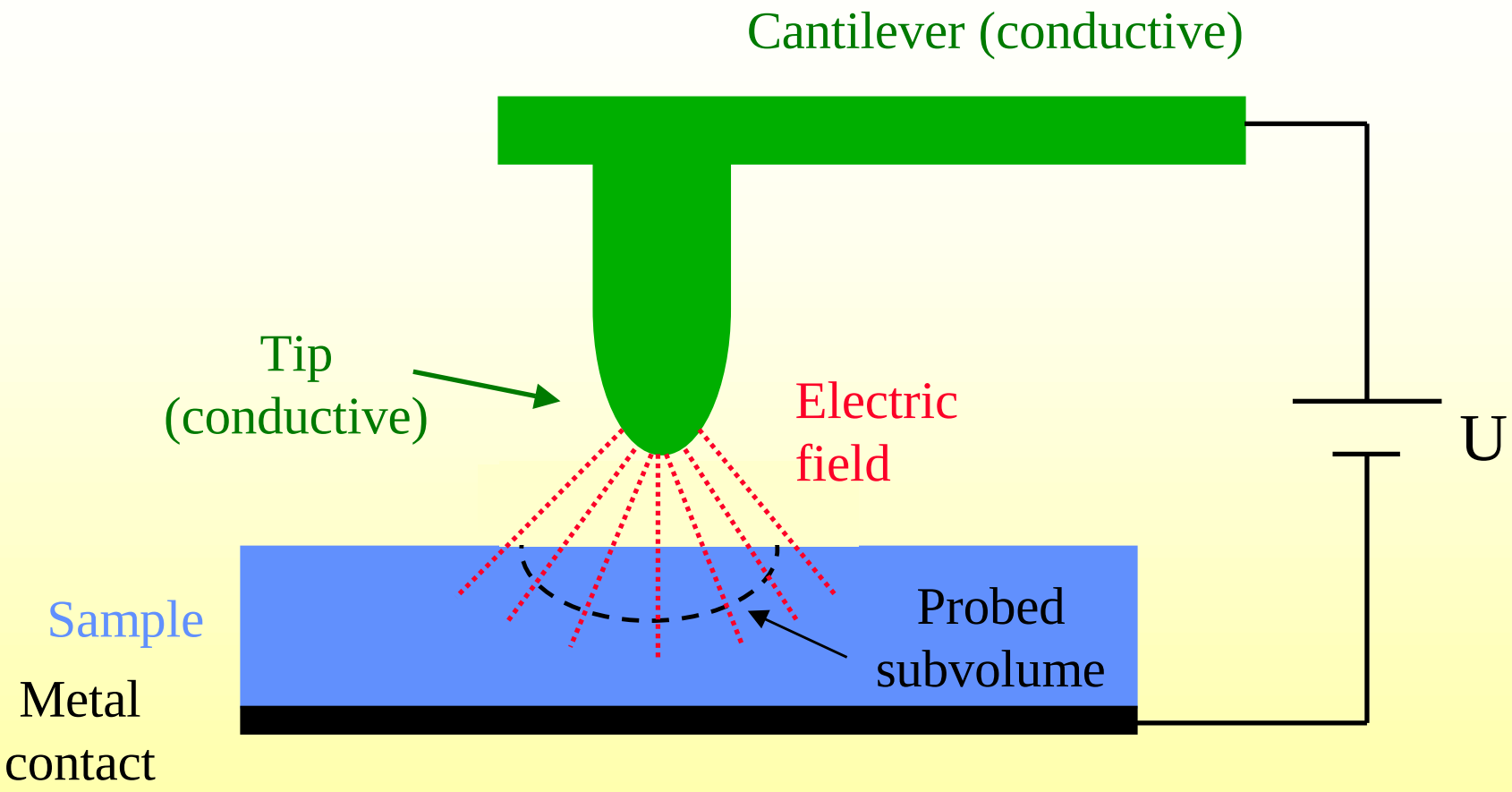
- Macroscopic conductivity spectroscopy
- Quasielastic neutron scattering
- Mechanical relaxation spectroscopy
- NMR relaxation techniques

Macroscopic averaging over the dynamics of more than 10^{20} mobile ions.

⟶ Loss of information about microscopic mechanisms

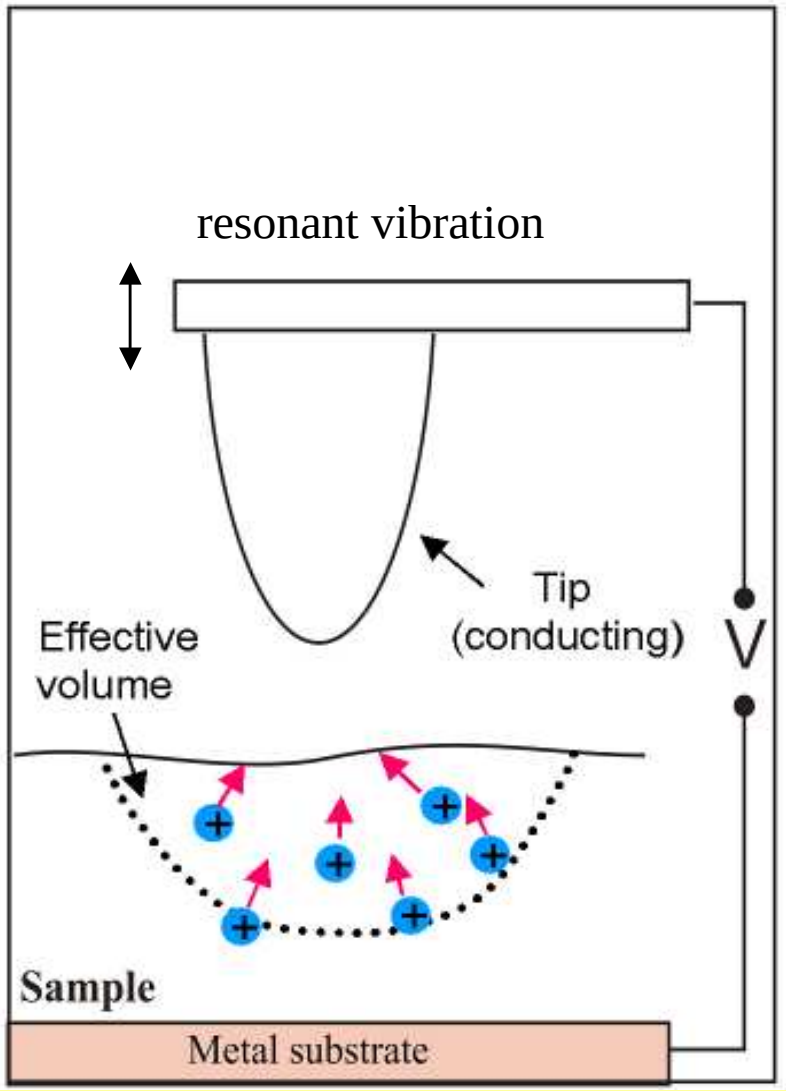
High loss of information in nano- and mesostructured materials:
Ion dynamics and transport in different phases and at interfaces.

Electrical force microscopy



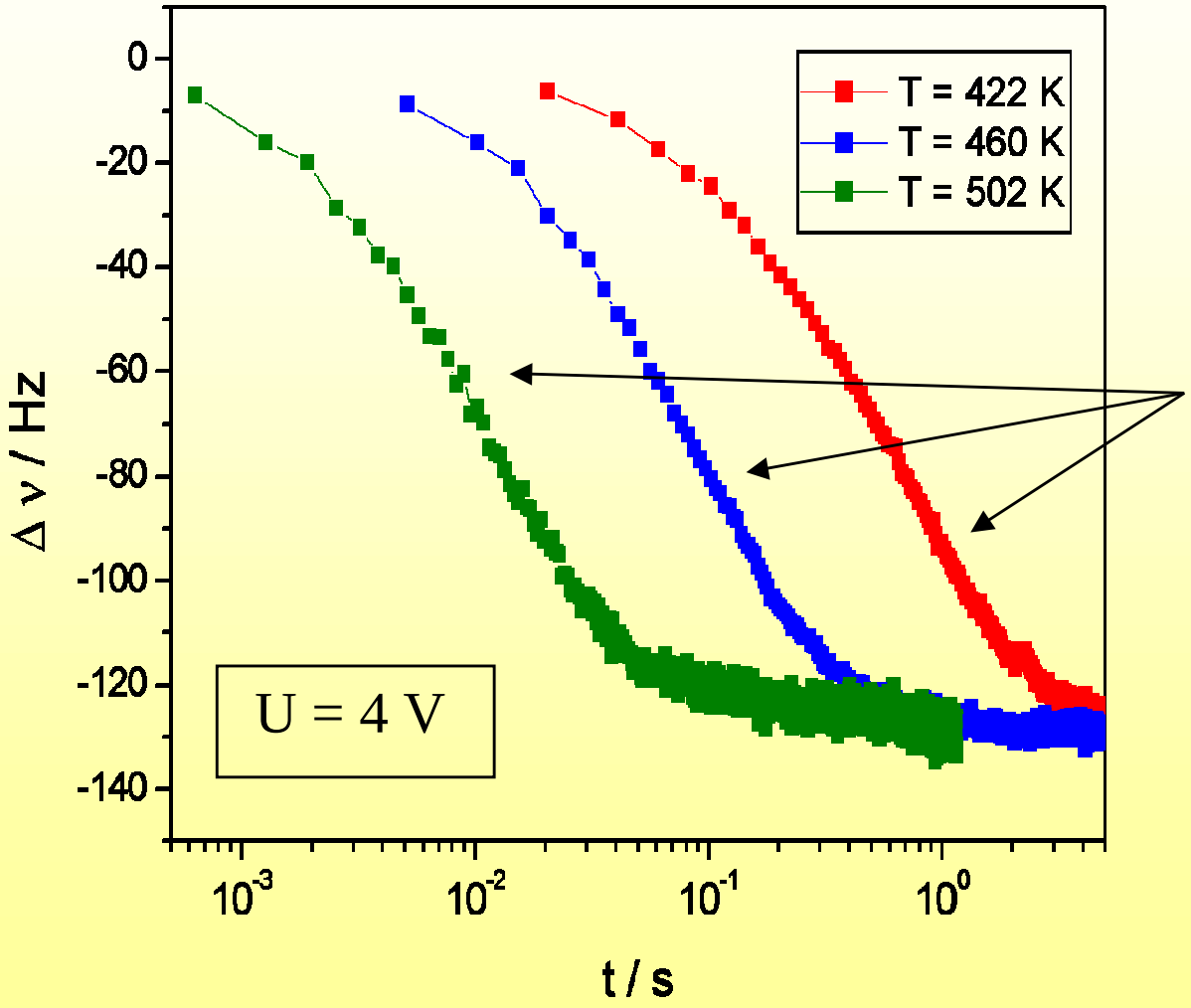
A large part of the voltage drop in the sample occurs in a small subvolume of the order (tip diameter)^3.

Electrostatic force spectroscopy



- Mobile ions move into field direction.
- Changes in the electrical forces between tip and sample.
- Changes in the resonant frequency of the cantilever.
- The ionic movements generate a counter field that impedes further ionic movements.
- The resonant frequency of the cantilever becomes constant.

Time dependence of the cantilever resonant frequency for a $K_2O * 2\ CaO * 4\ SiO_2$ glass



Decay due to thermally activated movements of K^+ ions

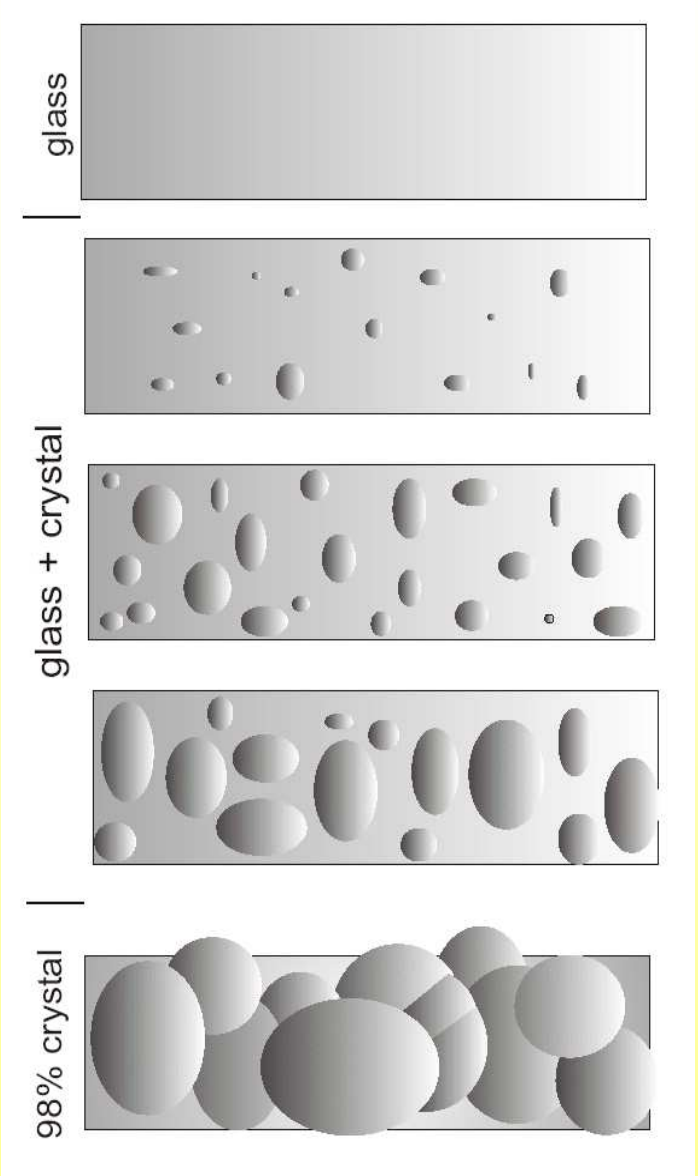
Spatially resolved spectroscopy on glass ceramics

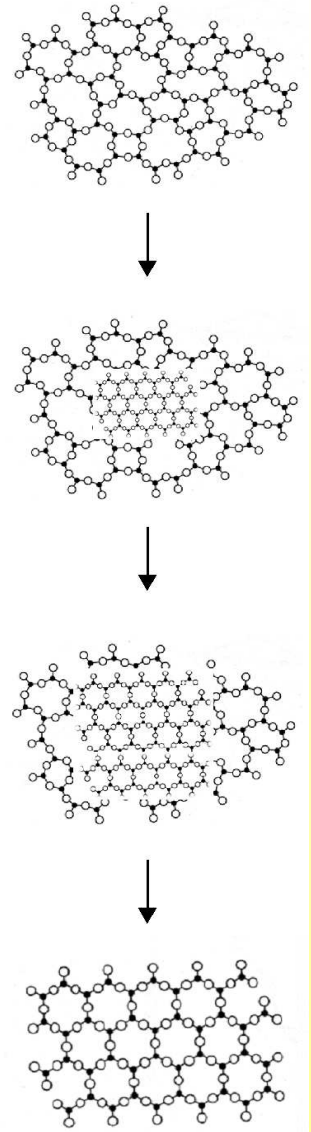
Increasing

annealing temperature

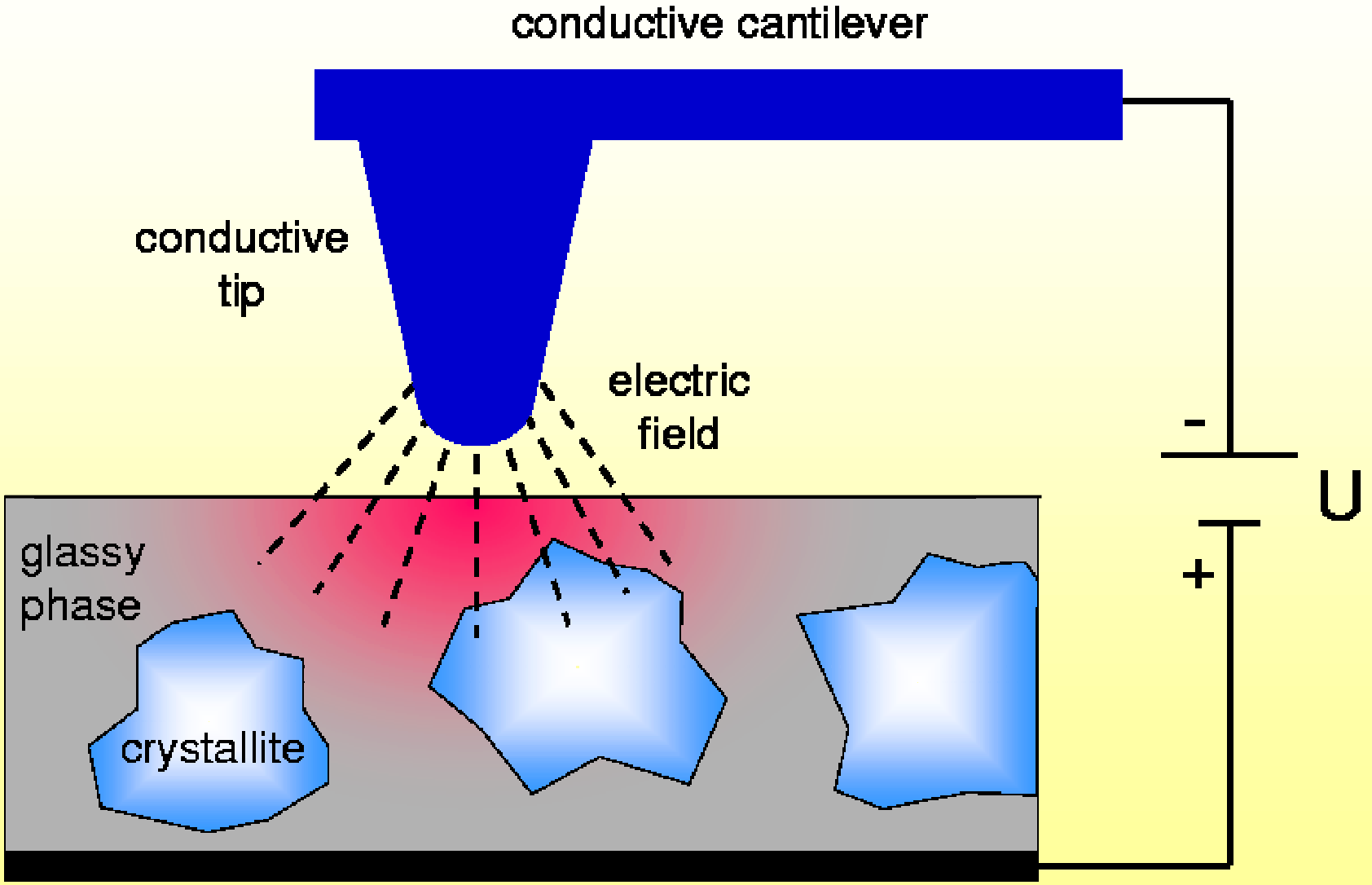
and/or

annealing time



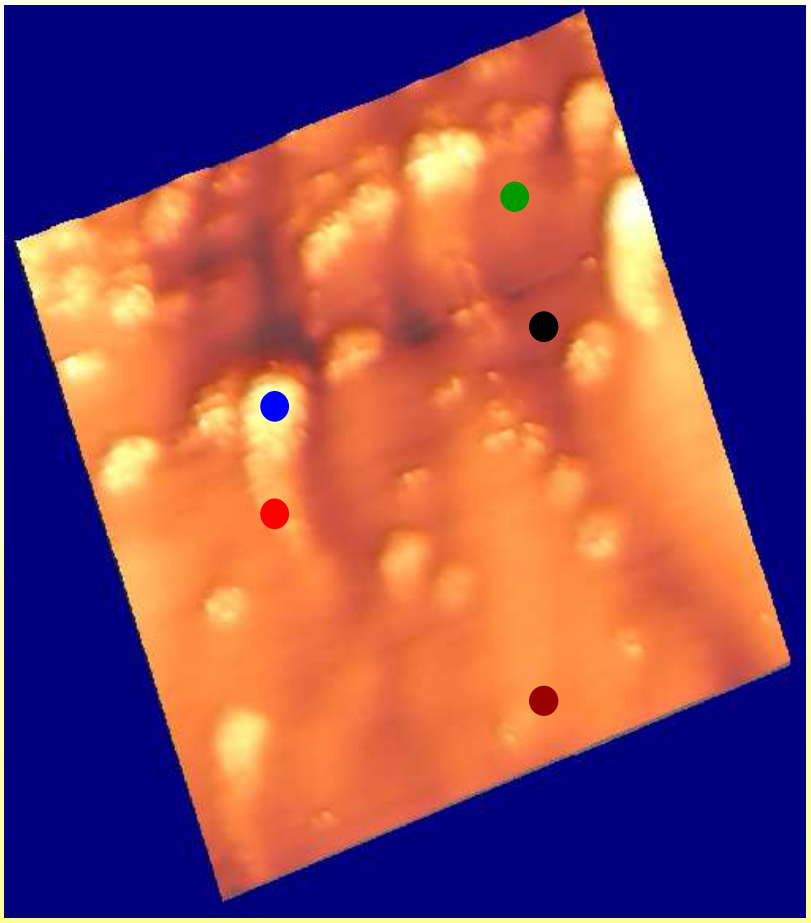


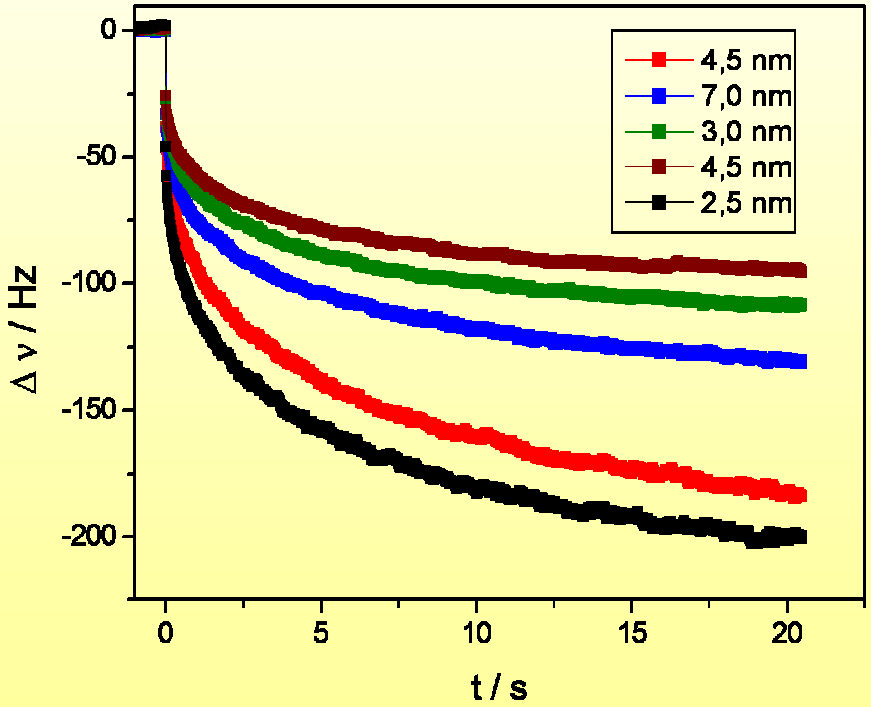
Electrostatic force spectroscopy on $Li_2O * Al_2O_3 * 2\ SiO_2$ glass ceramics



Glass ceramic with 78% crystallinity

444 nm x 444 nm





High relaxation strength: large amount of glassy phase

Low relaxation strength: large amount of crystalline phase

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