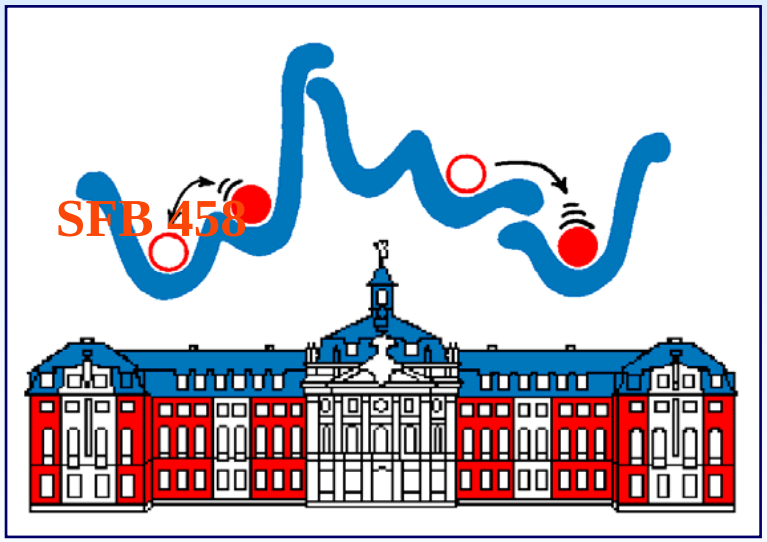
Ionic motion
in materials with disordered structures

Module 1 (includes Parts 1&2)

Klaus Funke, Münster



Many-particle dynamics
studied from picoseconds
to minutes and hours to
find rules for ionic motion
in disordered materials

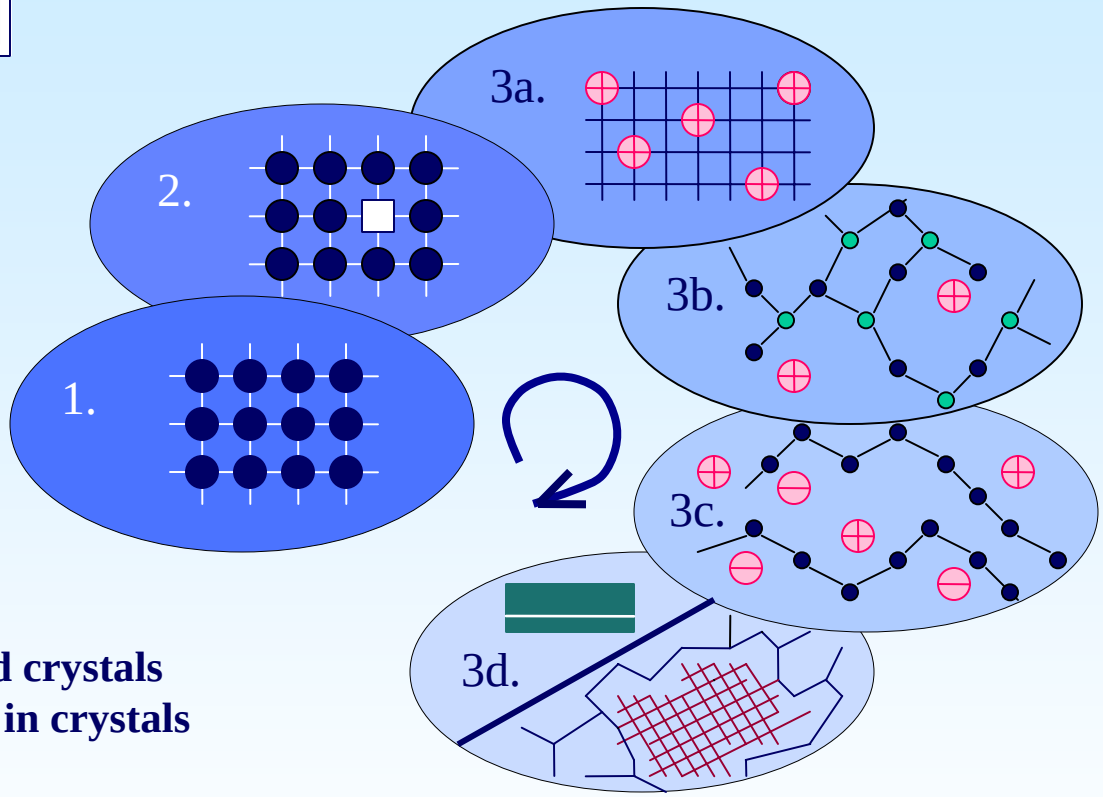
Glass Tutorial Series: prepared for and produced by the
International Material Institute for New Functionality in Glass
An NSF sponsored program – material herein not for sale
Available at www.lehigh.edu/imi

Delivered 5/5/06 at Lehigh University

Video Module 1 (includes Parts 1 &2)

1. Materials and phenomena : the rôle of disorder
2. Microscopy in time : $\sigma(\omega)$, $\varepsilon(\omega)$ and scaling properties
3. Dynamics of ions in motion : searching for simple rules

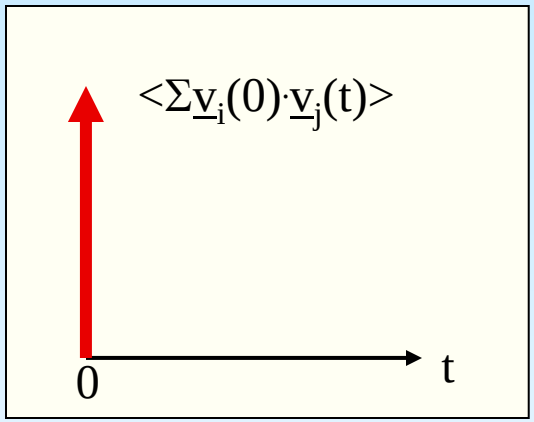
An evolving scheme of materials science

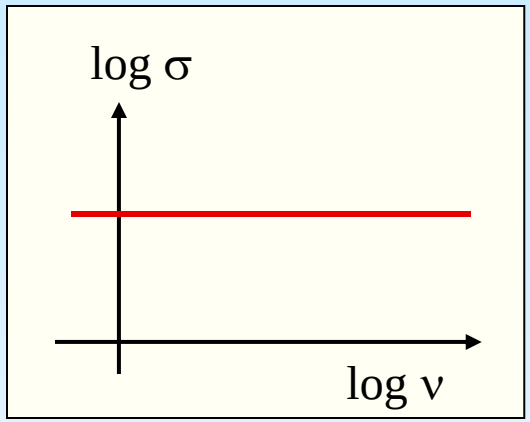


1. **Ideally ordered crystals**
2. **Point disorder in crystals**

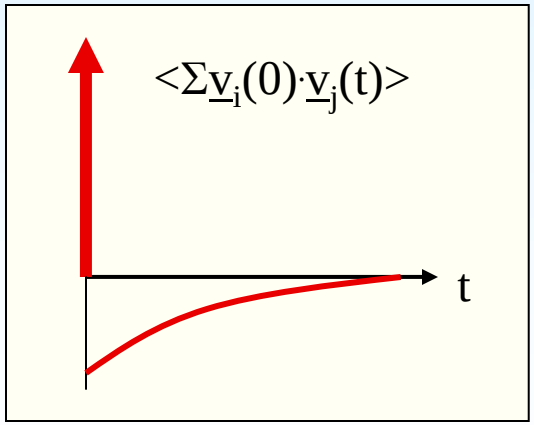
3a. Crystals with structural disorder
3b. Ion-conducting glasses
3c. Polymer electrolytes
3d. Thin-film systems, composite systems

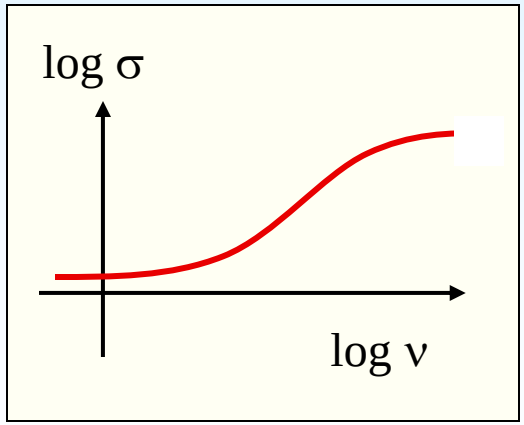
level two,
random hopping:



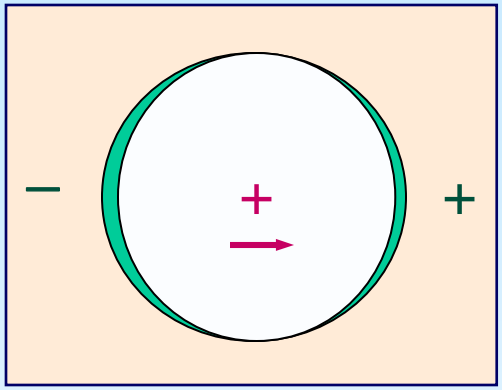


level three,
correlated hopping:



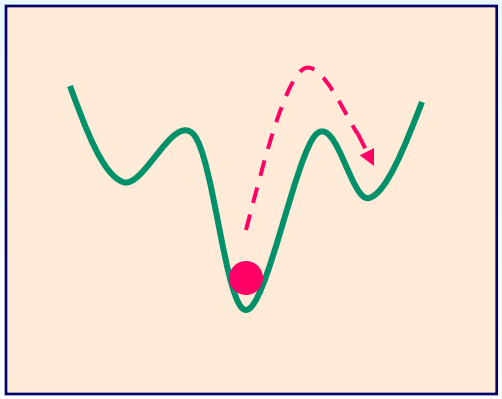


dilute strong
liquid electrolyte:



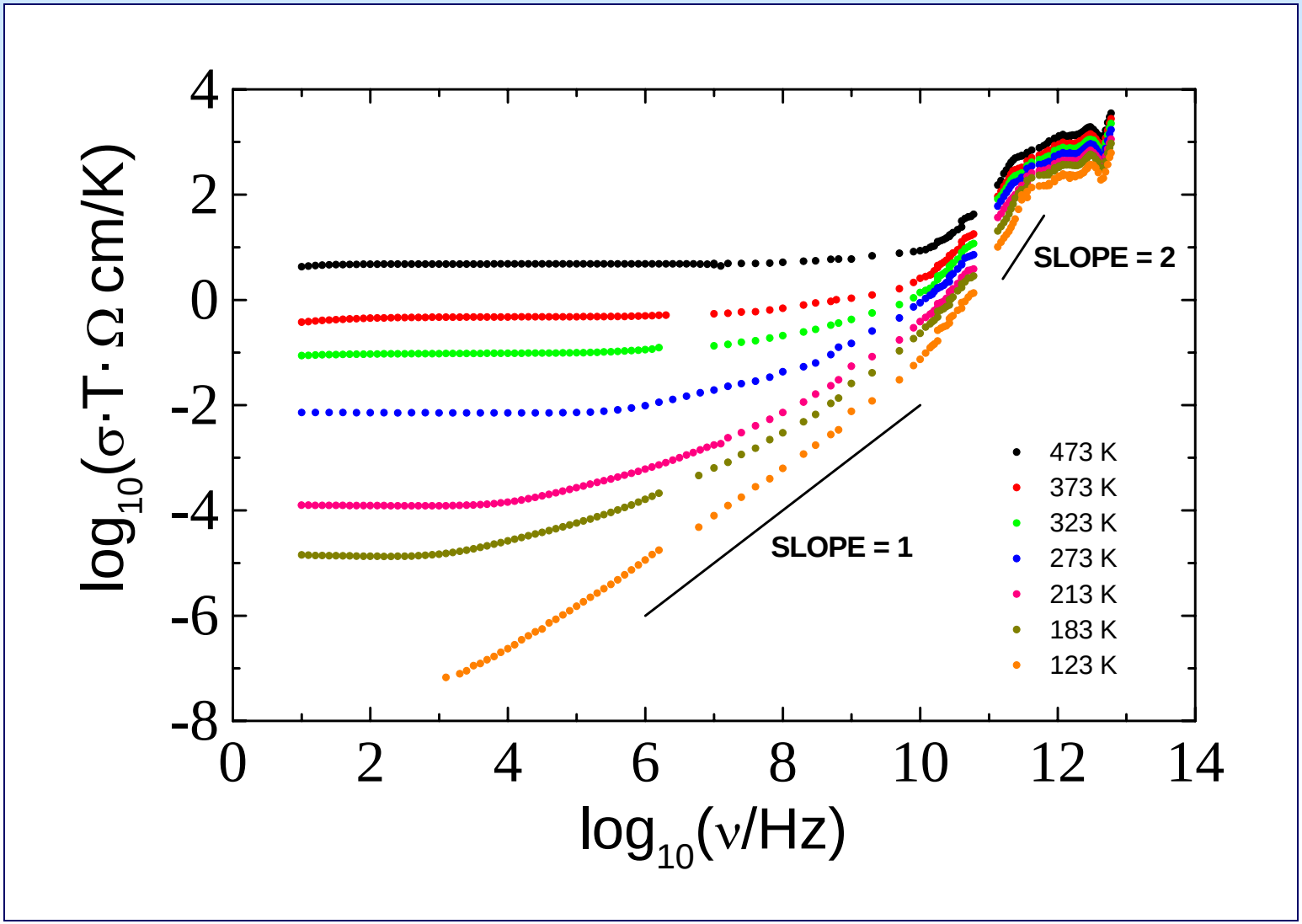
dispersion
in $\sigma(\omega)$
hardly
visible

solid electrolyte
with structural
disorder:



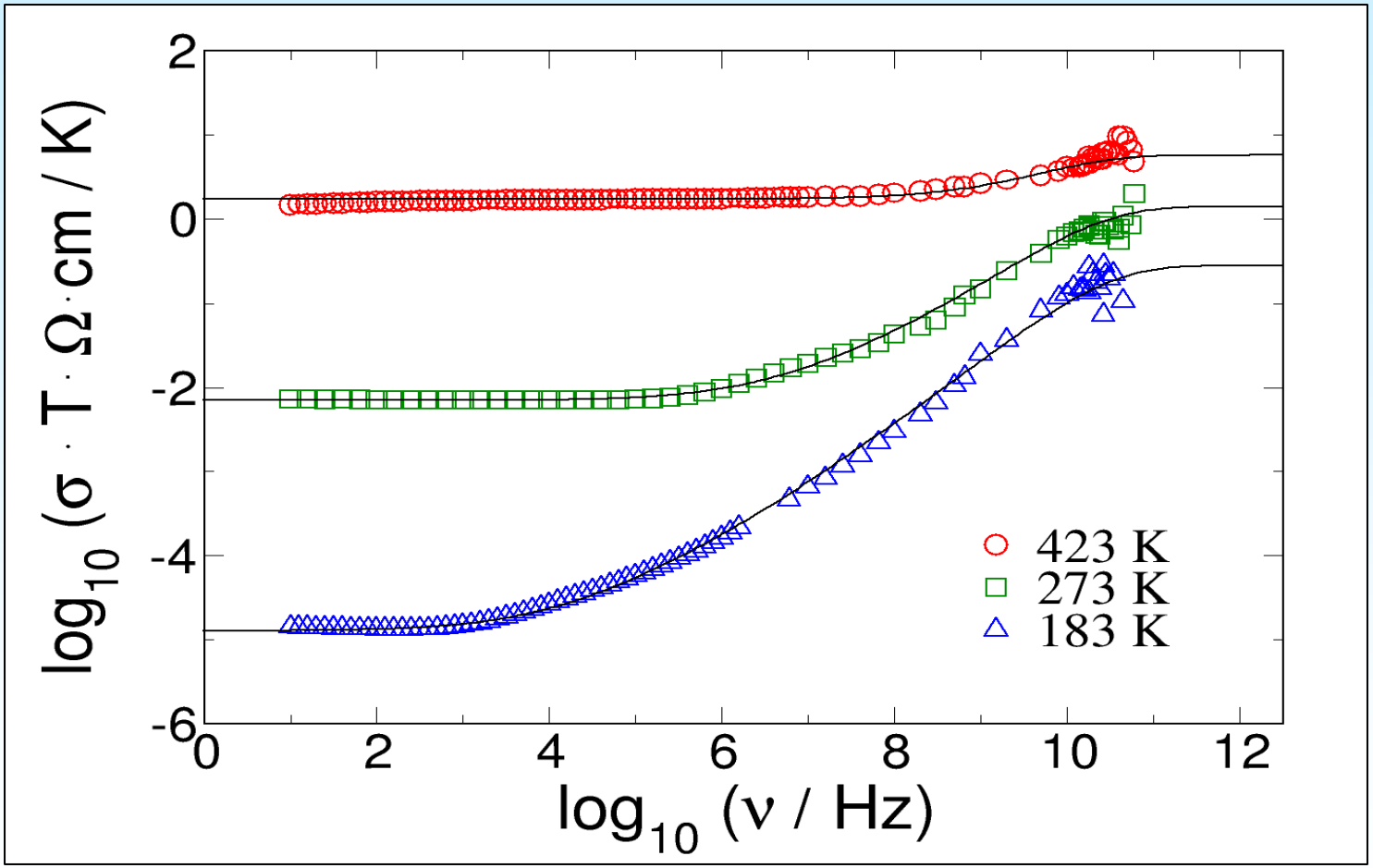
dispersion
over many
decades in
conductivity

$Ag_2S \cdot GeS_2$ glassy electrolyte, from 123 K to 473 K



$Ag_2S \cdot GeS_2$ glassy electrolyte:

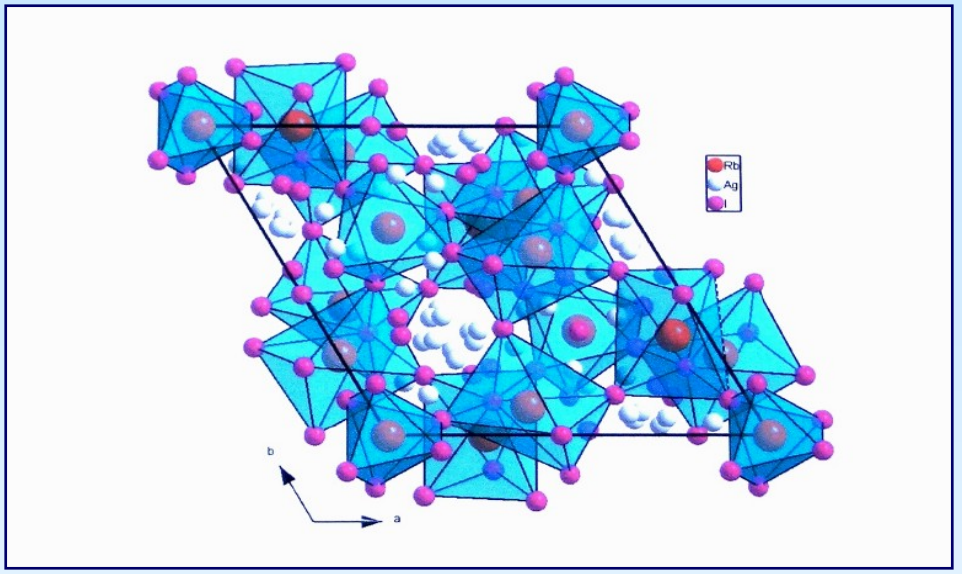
vibrational contribution removed, set of model spectra included



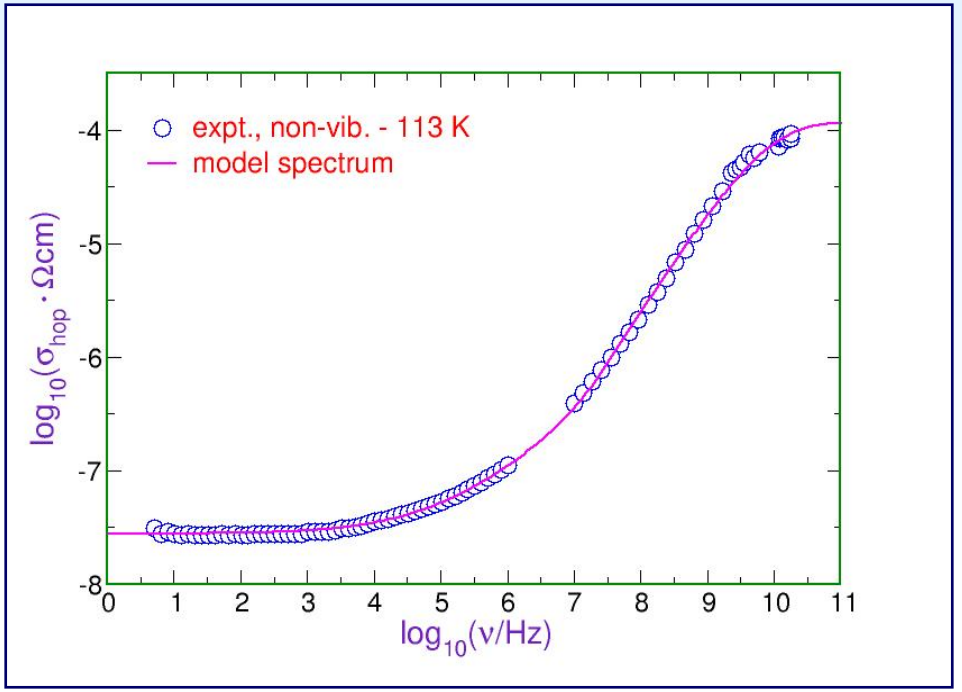
$\sigma(0)\cdot T$ and $\sigma(\infty)\cdot T$ both Arrhenius activated

γ – $Rb\,Ag_4\,I_5$

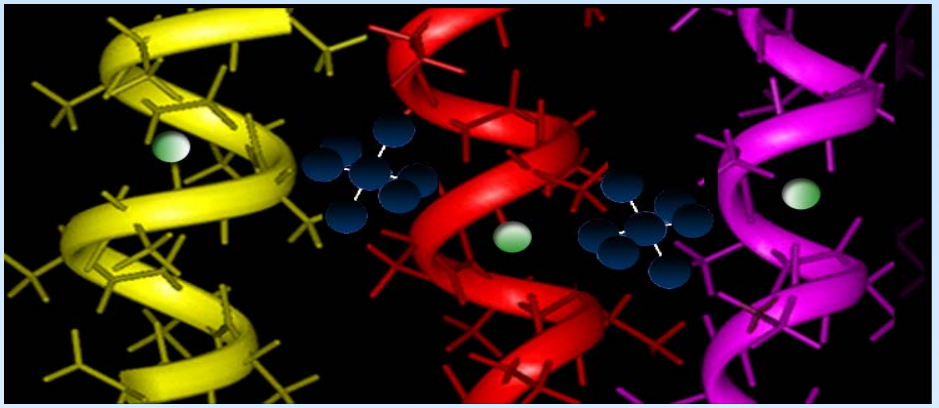
crystal structure .....



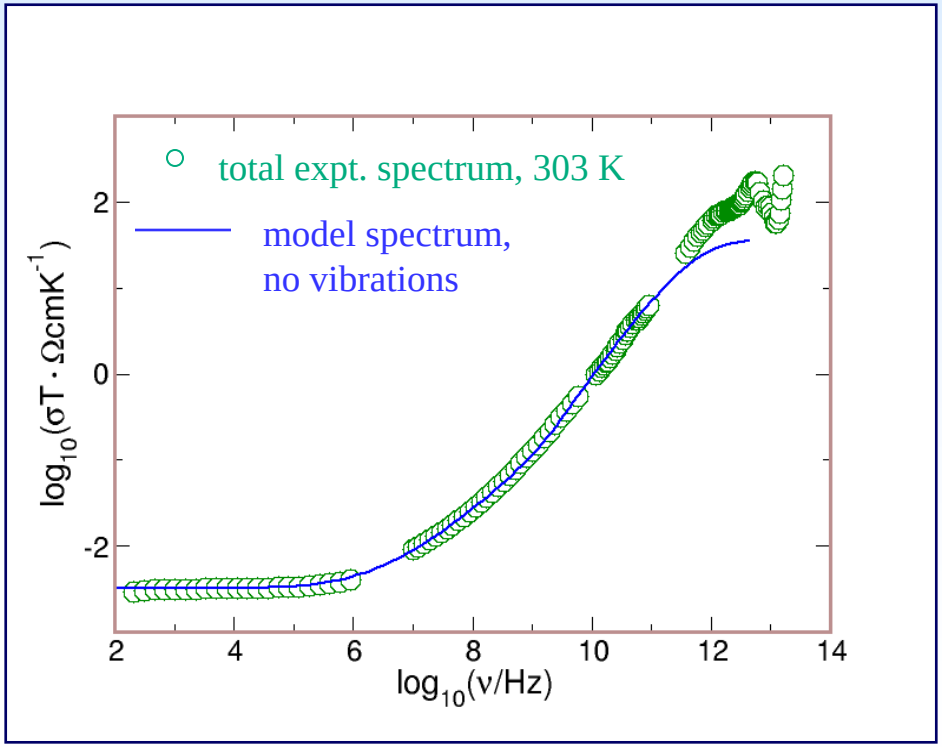
conductivity spectrum
(vibrations removed)
at 113 K .....



Salt-in-polymer electrolyte (1 molal $NaPF_6$ in a polyurethane)



conductivity spectrum (including vibrations) at 303 K .....

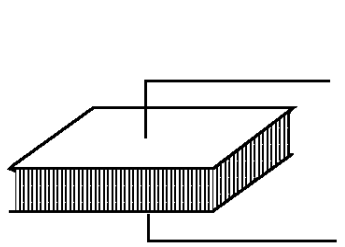


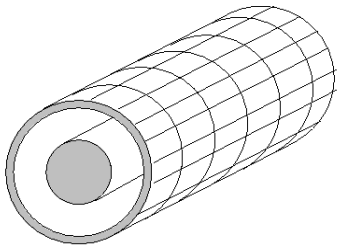
1. Materials and phenomena : the rôle of disorder

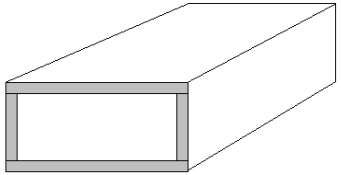
2. Microscopy in time : $\sigma(\omega)$, $\varepsilon(\omega)$ and scaling properties

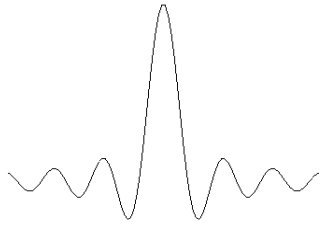
3. Dynamics of ions in motion : searching for simple rules

Measuring conductivity spectra, σ (ω), and permittivity spectra, ε (ω) :









$\approx 10^{-3}$ Hz..... $\approx 10^{6}$ Hz ..... $\approx 10^{10}$ Hz..... $\approx 10^{11}$ Hz..... $\approx 10^{14}$ Hz

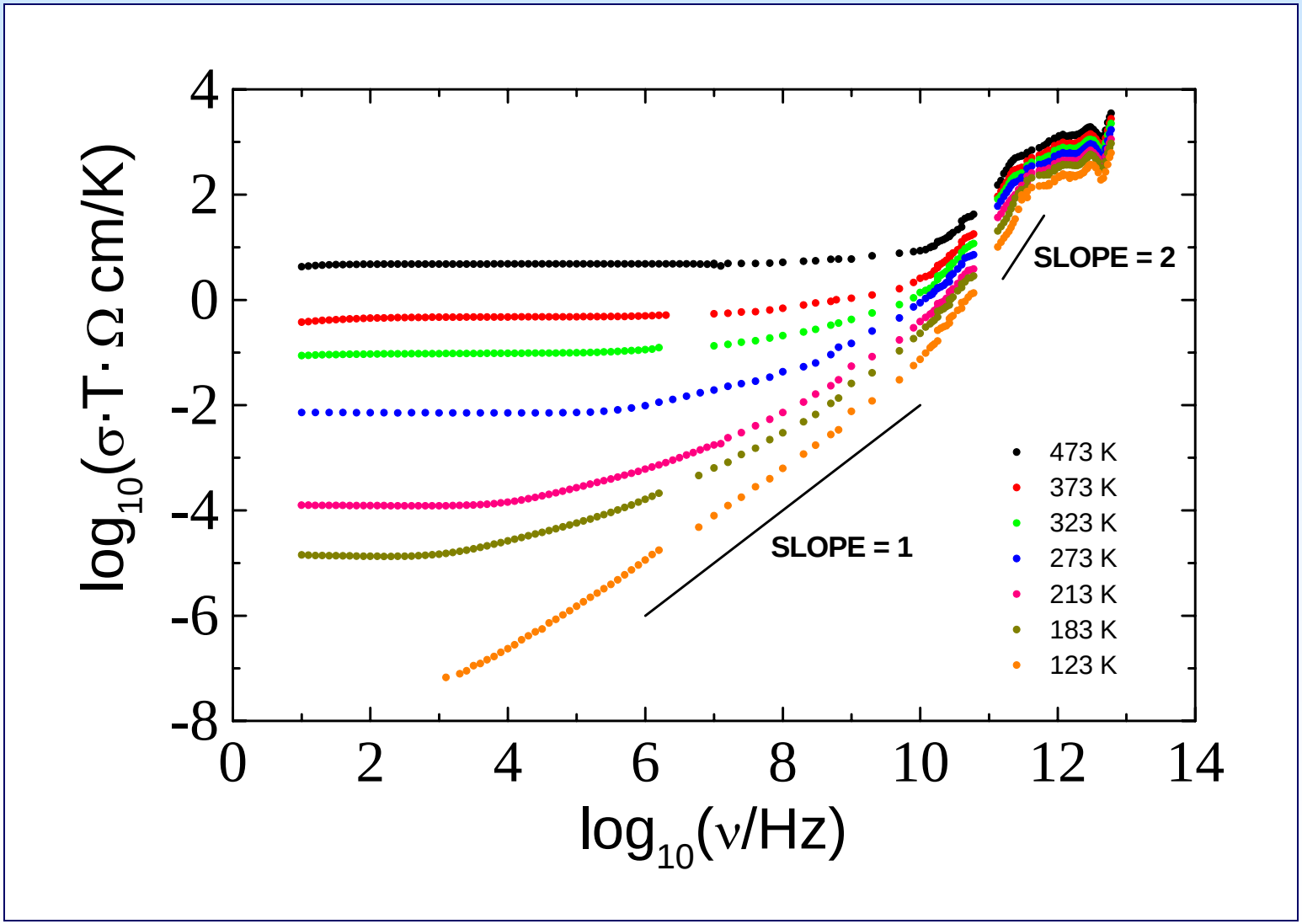
Impedance Spectrometer	Coaxial Waveguides	Rectangular Waveguides	FTIR Spectrometer

Measured quantities: amplitudes and phases of transmitted or reflected waves

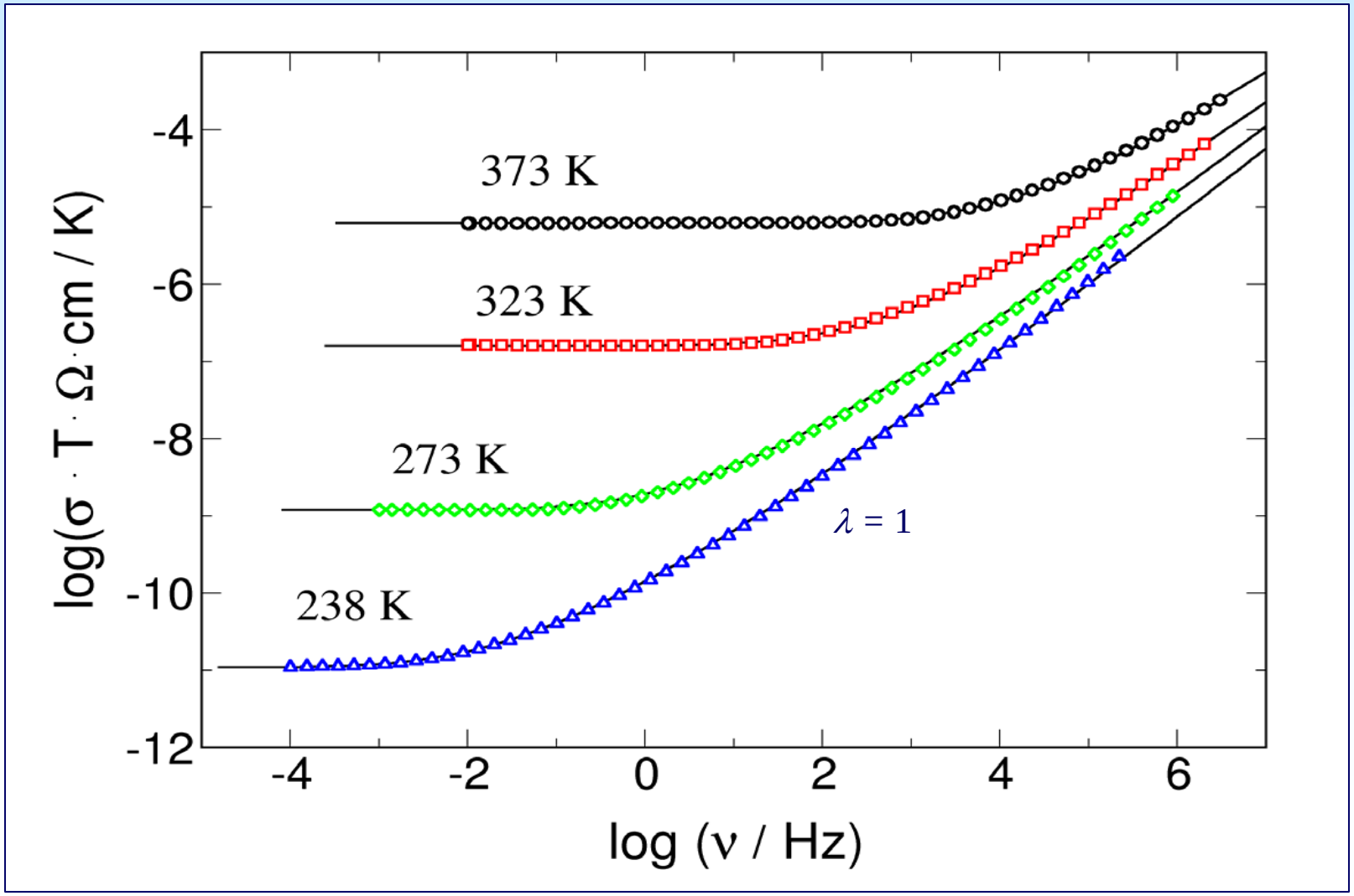
Basis for evaluation: Maxwell‘s equations plus boundary conditions

→ $\hat{\sigma}(\omega) = i\omega\varepsilon_0\hat{\varepsilon}(\omega)$ → $\sigma(\omega) = \mathrm{Re}\,\hat{\sigma}(\omega)$ and $\varepsilon(\omega) = \mathrm{Re}\,\hat{\varepsilon}(\omega)$

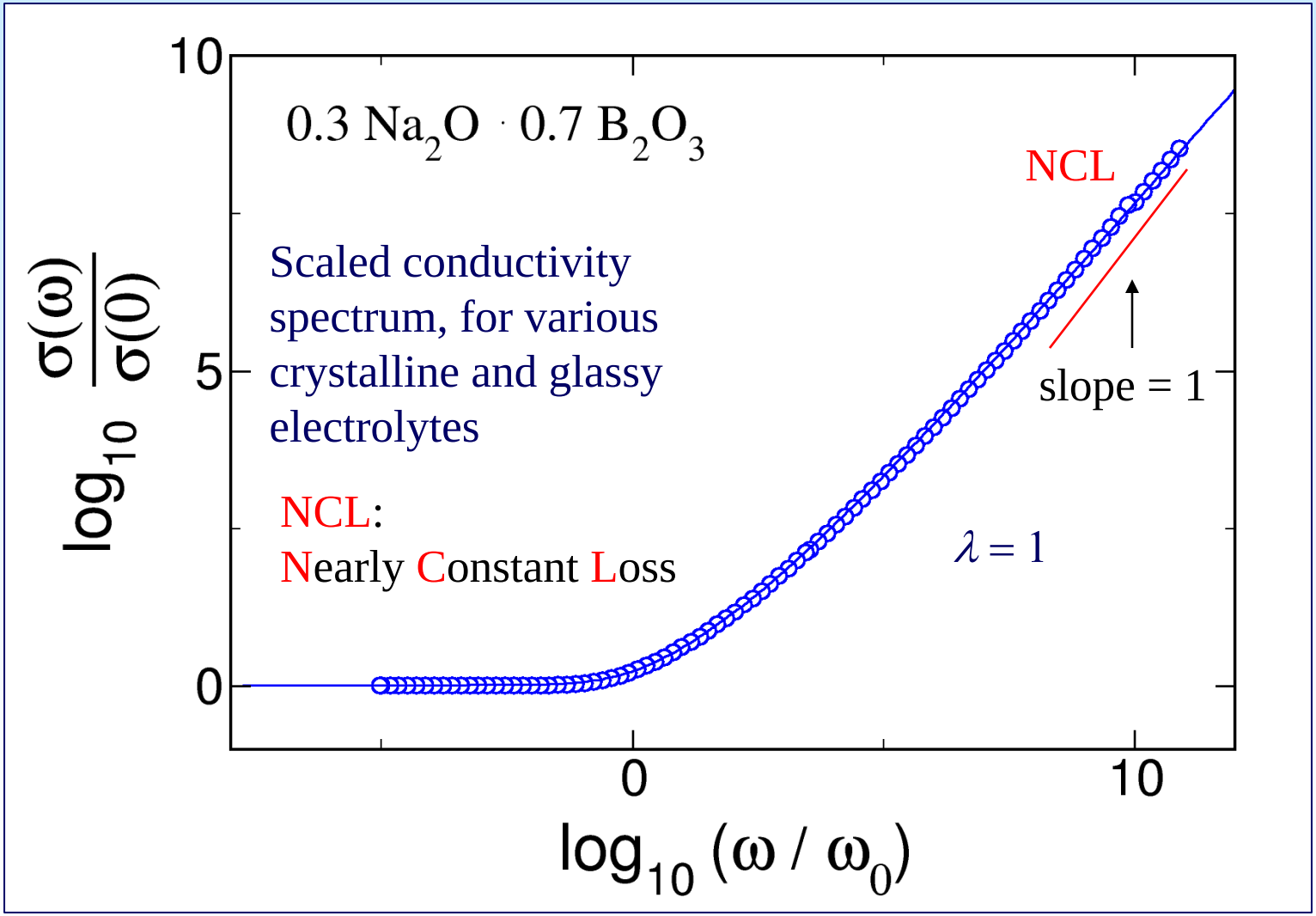
$Ag_2S \cdot GeS_2$ glassy electrolyte, from 123 K to 473 K



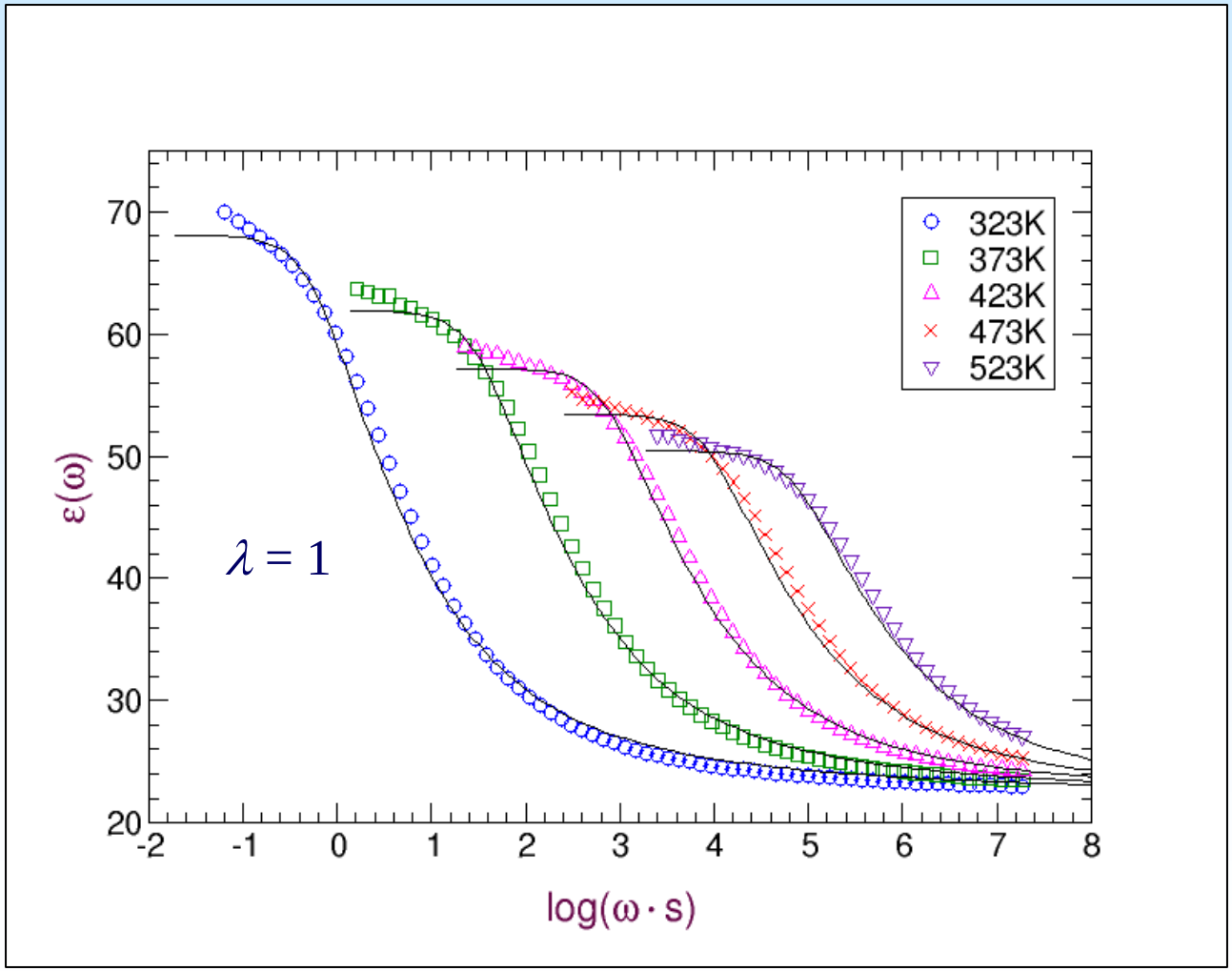
Conductivity isotherms for glassy 0.3 $Li_2O \cdot 0.7\ B_2O_3$



Gradual transition into NCL behavior :

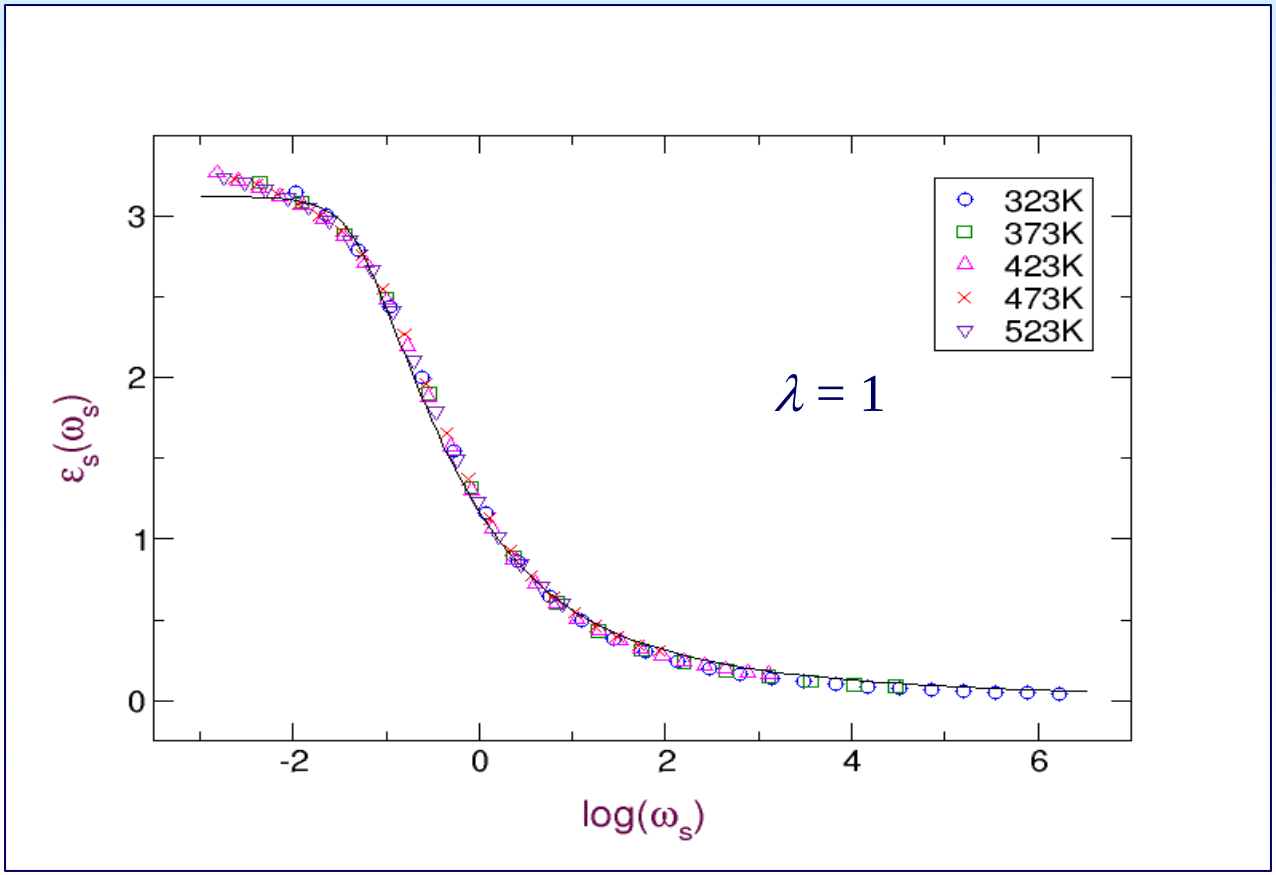


$0.2\ Na_2O \cdot 0.8\ GeO_2$ glass, permittivity isotherms



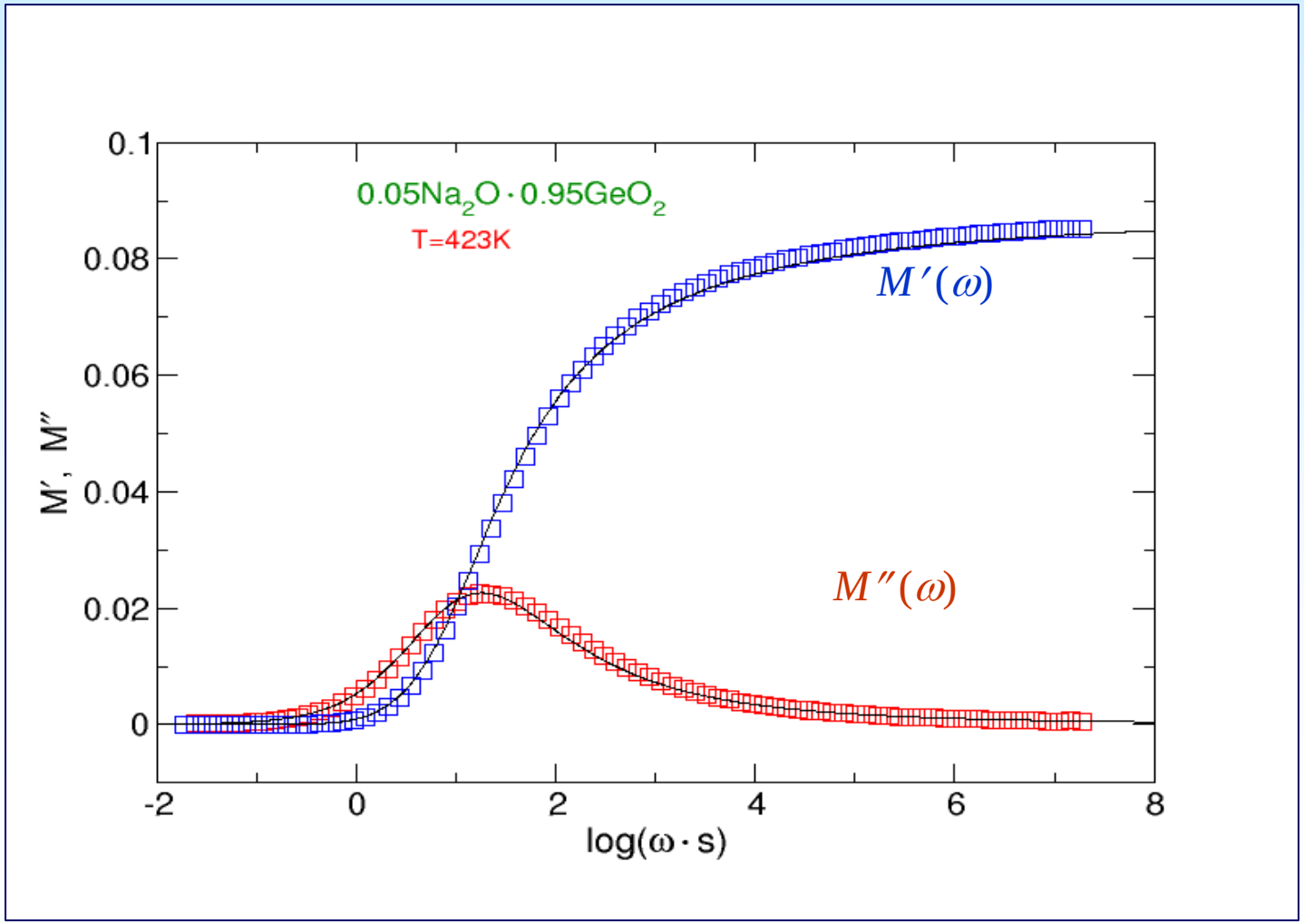
Scaled permittivity for 0.2 $Na_2O \cdot 0.8\ GeO_2$ glass

$$\varepsilon_S(\omega_S) = \frac{\omega_0 \cdot \varepsilon_0 \cdot (\varepsilon(\omega_S) - \varepsilon(\infty))}{\sigma(0)} = \frac{1}{\omega_S} \cdot \mathrm{Im}\,\hat{\sigma}_S(\omega_S)$$



Real and imaginary parts of dielectric modulus do NOT scale

$$\hat{M}(\omega) = M'(\omega) + iM''(\omega) = \frac{1}{\hat{\varepsilon}(\omega)}$$



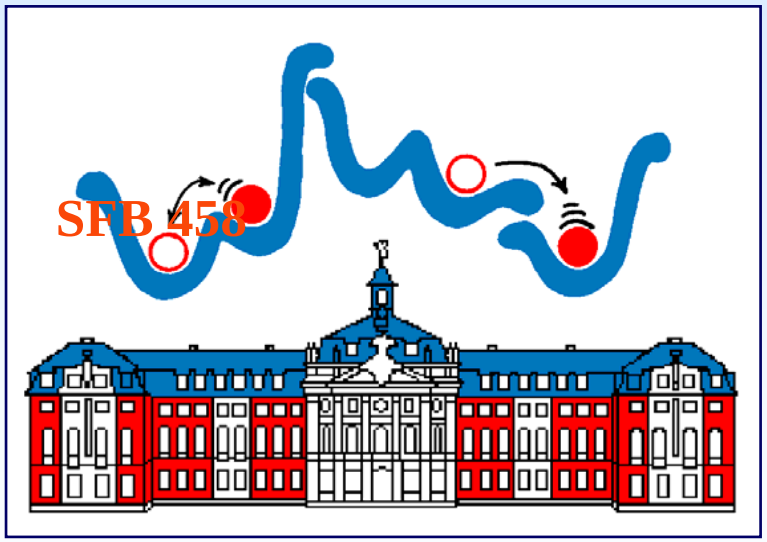
This lecture continues on a 2nd module -

Video Module 2 : Dynamics of Ions (Part 3)

Ionic motion
in materials with disordered structures

Video Module 2 (Part 3- Dynamics of Ions)

Klaus Funke, Münster



Many-particle dynamics
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Video Module 2 : Dynamics of Ions (includes Part 3)

1. Materials and phenomena : the rôle of disorder
2. Microscopy in time : $\sigma(\omega)$, $\varepsilon(\omega)$ and scaling properties
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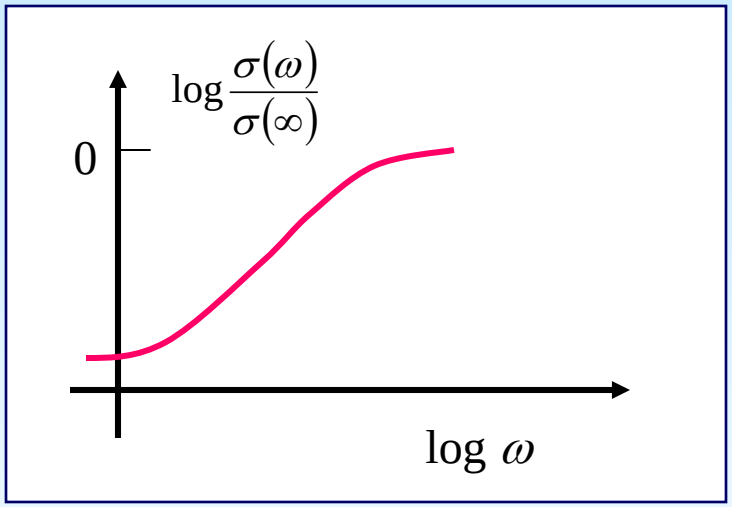
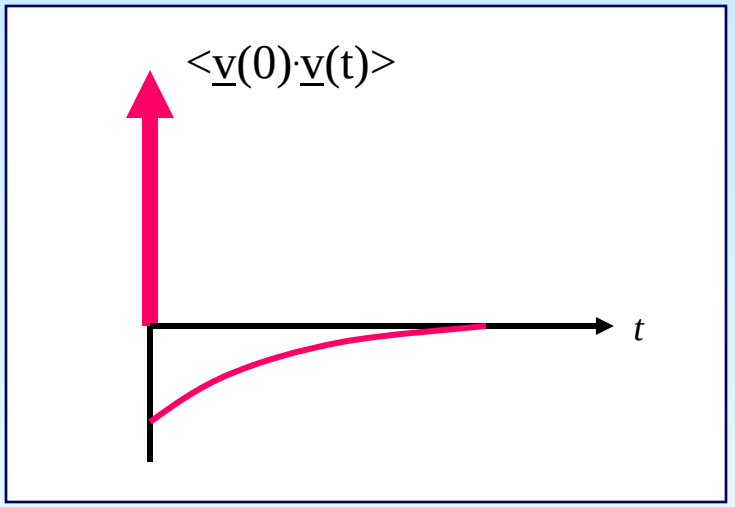
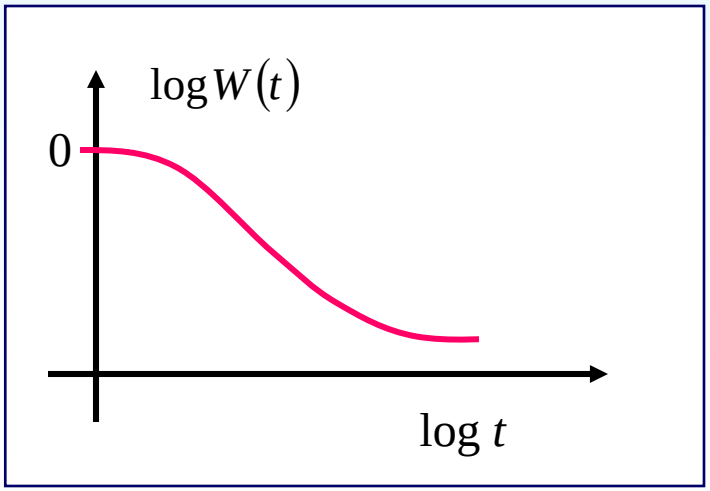
Introducing the time-dependent correlation factor, $W(t)$

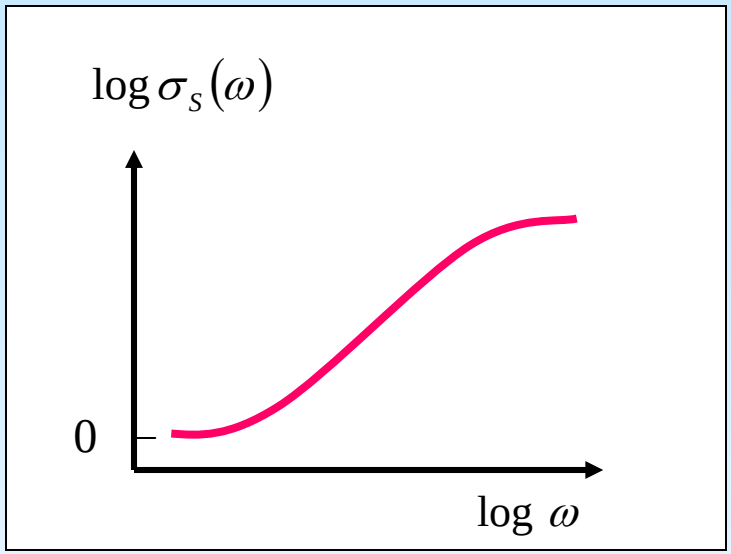


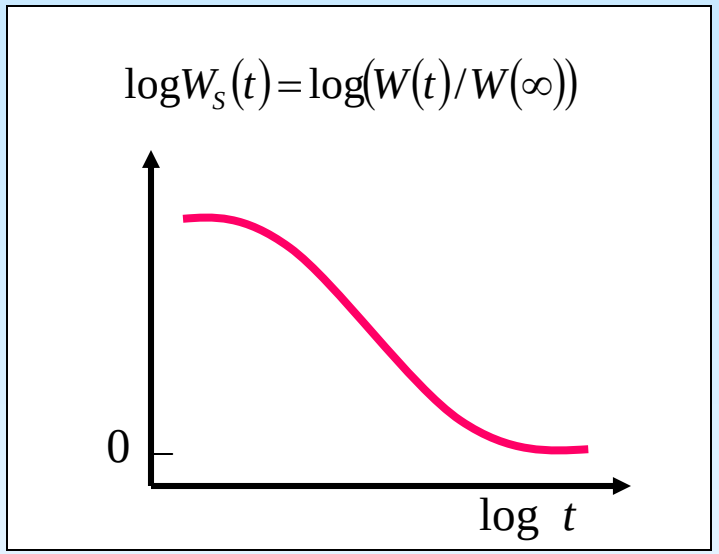




$$\frac{\sigma(\omega)}{\sigma(\infty)} = 1 + \int_0^\infty \dot{W}(t) \cdot \cos(\omega \cdot t) \cdot dt$$

$$\frac{\hat{\sigma}_{HOP}(\omega)}{\sigma(\infty)} = 1 + \int_0^\infty \dot{W}(t) \cdot \exp(-i\omega \cdot t) \cdot dt$$



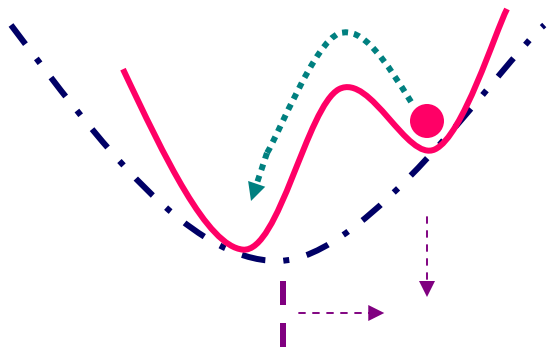


$$\hat{\sigma}_S(\omega) = \frac{\hat{\sigma}_{HOP}(\omega)}{\sigma(0)} = 1 + i\omega\int_0^\infty (W_S(t) - 1)\cdot\exp(-i\omega\cdot t)\cdot dt$$

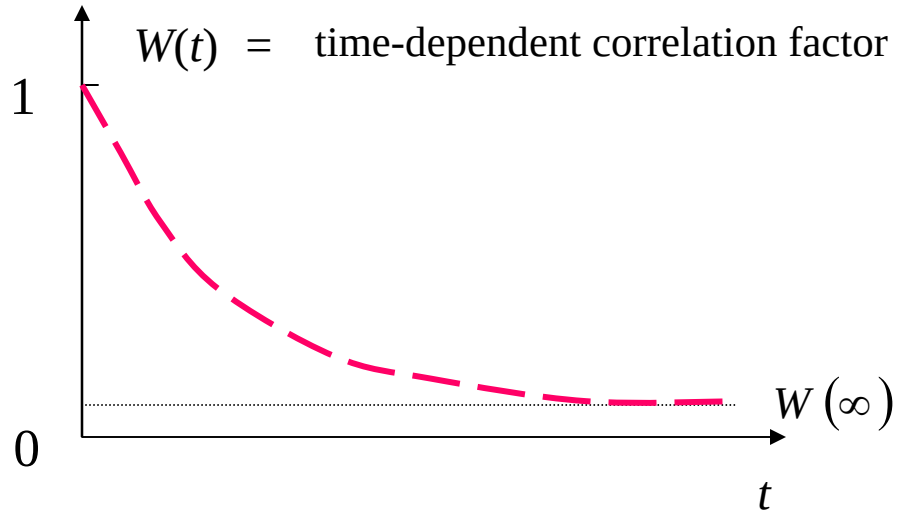
As soon as $W_S(t)$ is known, the scaled conductivity is also known. Very realistic results are obtained by the MIGRATION concept, the acronym standing for MIsmatch Generated Relaxation for the Accommodation and Transport of IONs

In the model, ω_0 marks the onset of the dispersion.
Scaled time: $t_S = t\omega_0$, scaled frequency: $\omega_S = \omega/\omega_0$

single-particle route



many-particle route



$$-\frac{\dot{W}(t)}{W(t)} = -B \cdot \dot{g}(t) \quad [+\Gamma_0]$$

$$-\frac{\dot{g}(t)}{g(t)} = \Gamma_0 \cdot W(t) \cdot N(t)$$

$$N(t) - N(\infty) = (B \cdot g(t))^{\lambda}$$

⬅ if motion is completely localised

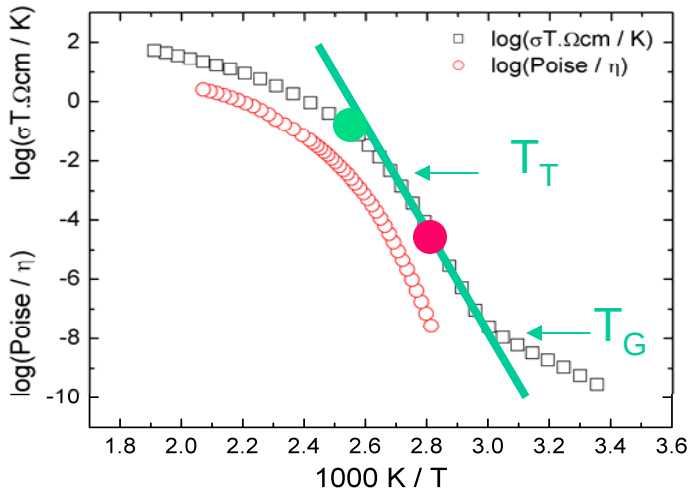
$W(t)$ = correlation factor	$W(t)$ and $W_S(t_S)$
$g(t)$ = mismatch function	$\sigma(\omega)$ and $\sigma_S(\omega_S)$
$N(t)$ = number function	$\varepsilon(\omega)$ and $\varepsilon_S(\omega_S)$

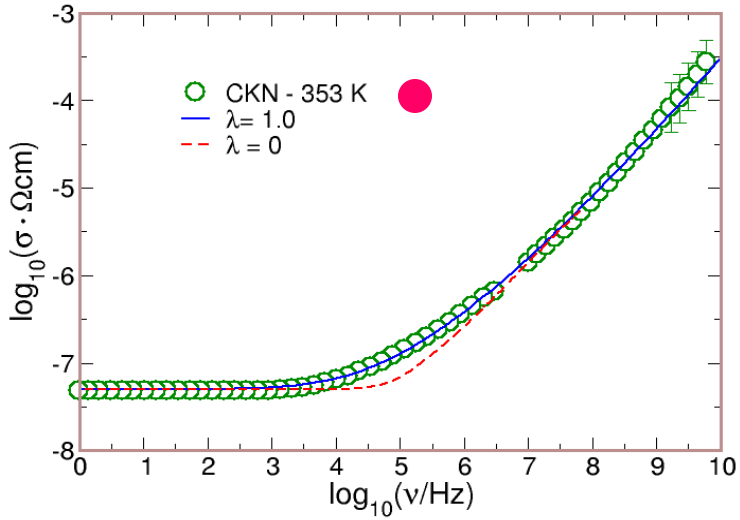
In 0.4 $Ca(NO_3)_2$ 0.6 KNO_3 (CKN)

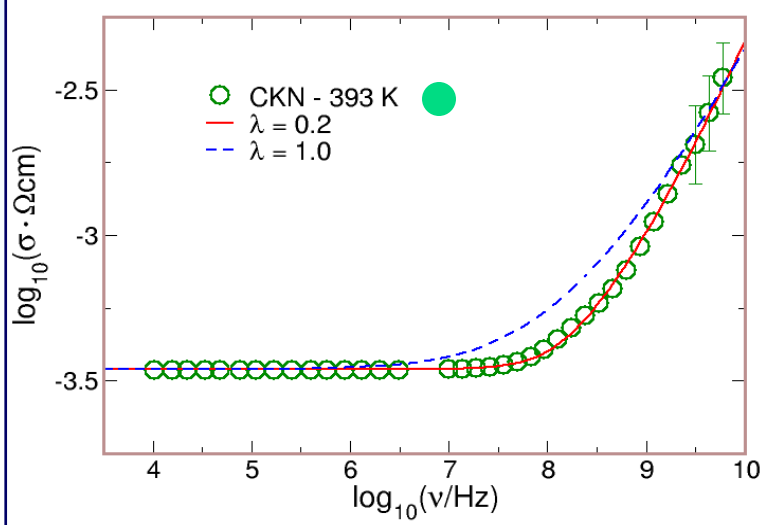
above T_G

$K = \lambda + 1$ changes

from 2.0 to 1.2

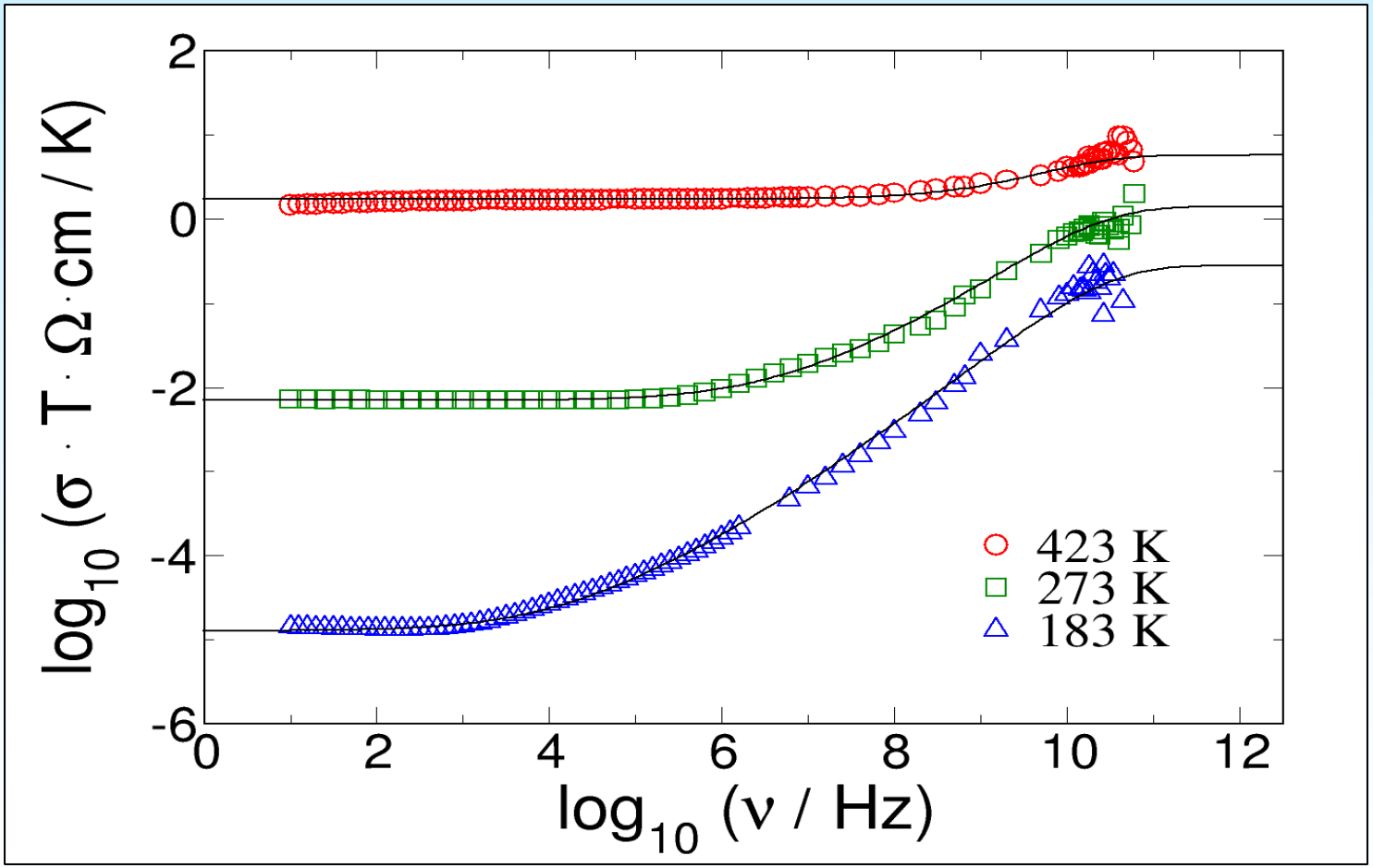






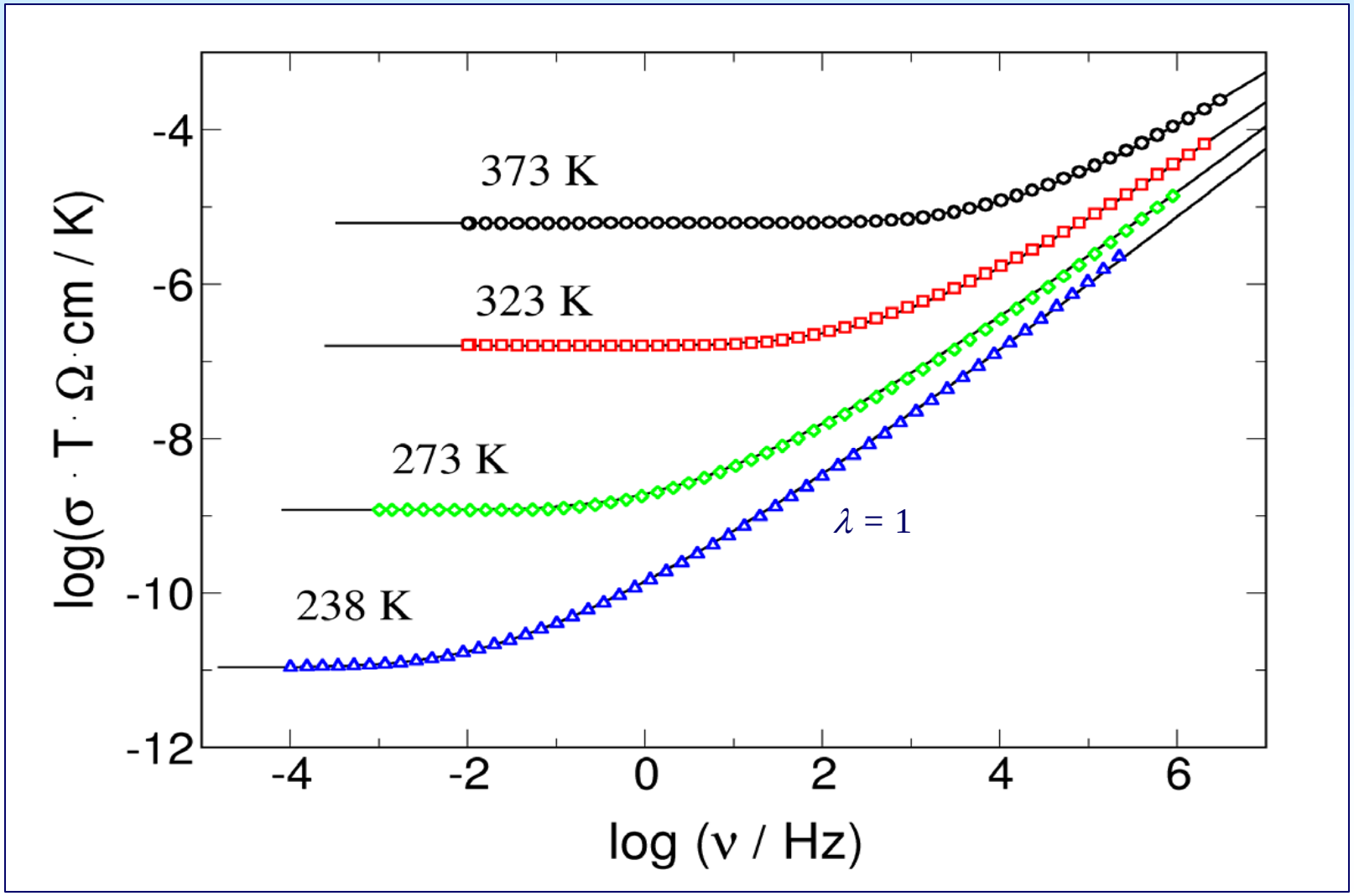
$Ag_2S \cdot GeS_2$ glassy electrolyte:

vibrational contribution removed, set of model spectra included

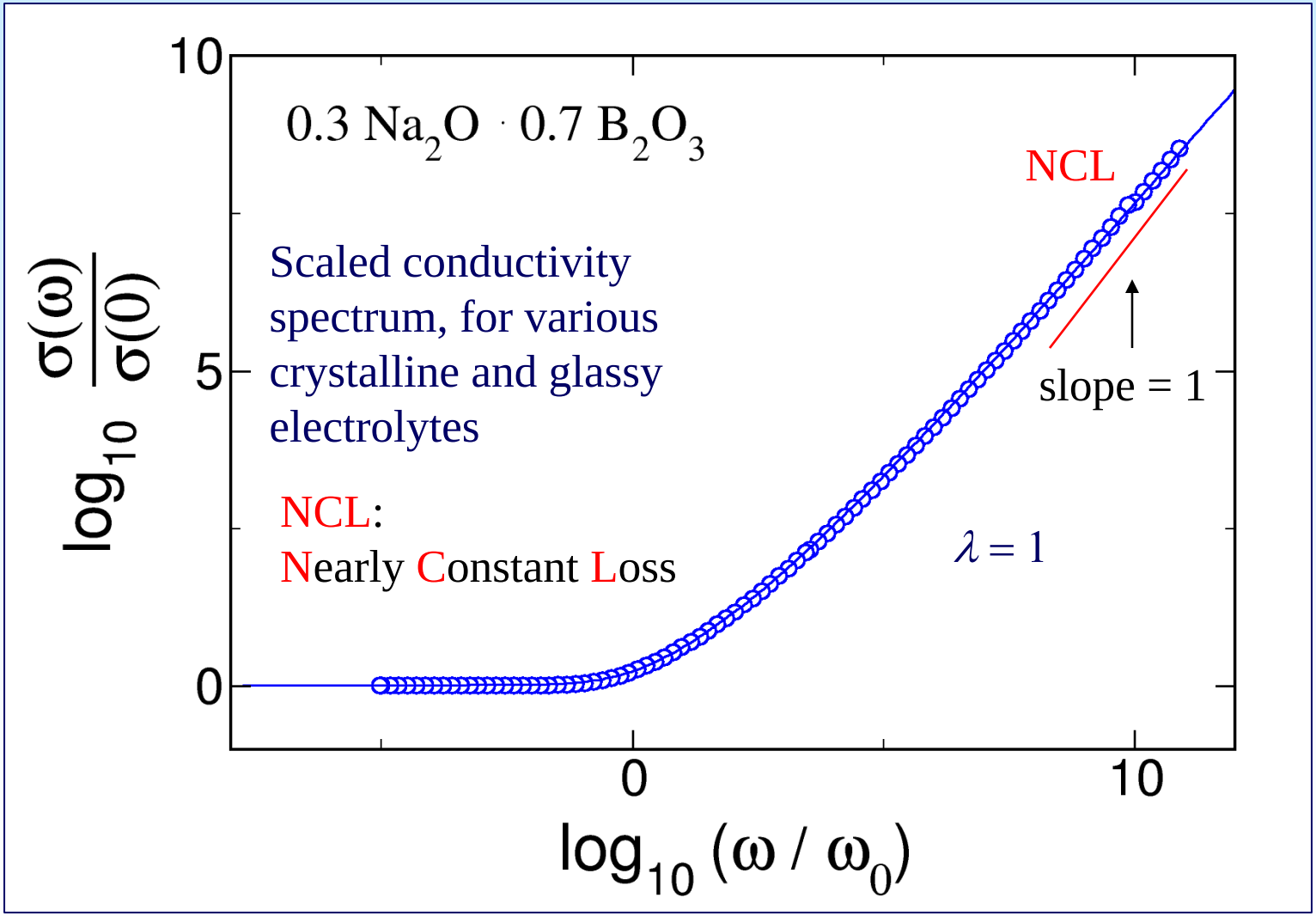


$\sigma(0)\cdot T$ and $\sigma(\infty)\cdot T$ both Arrhenius activated

Conductivity isotherms for glassy 0.3 $Li_2O \cdot 0.7\ B_2O_3$

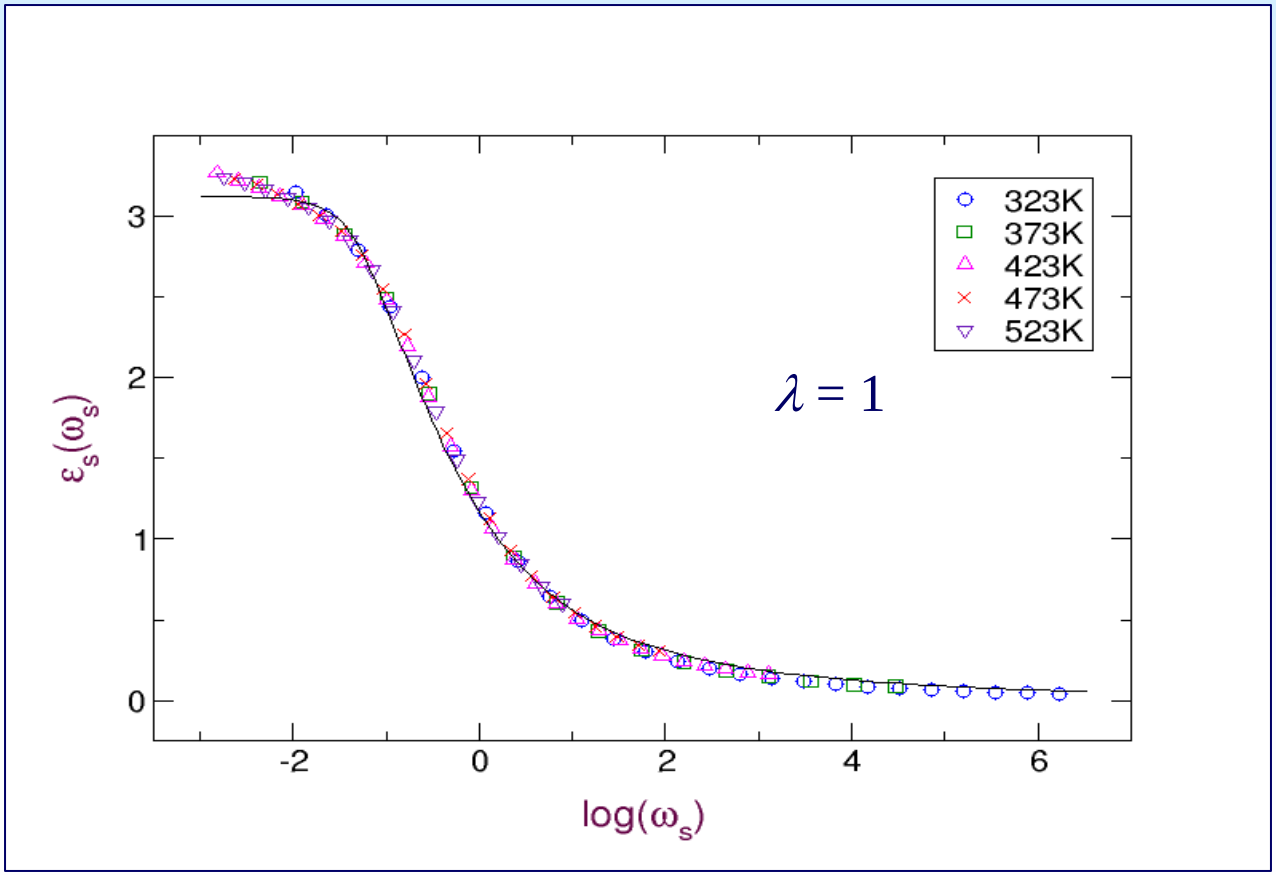


Gradual transition into NCL behavior :



Scaled permittivity for 0.2 $Na_2O \cdot 0.8\ GeO_2$ glass

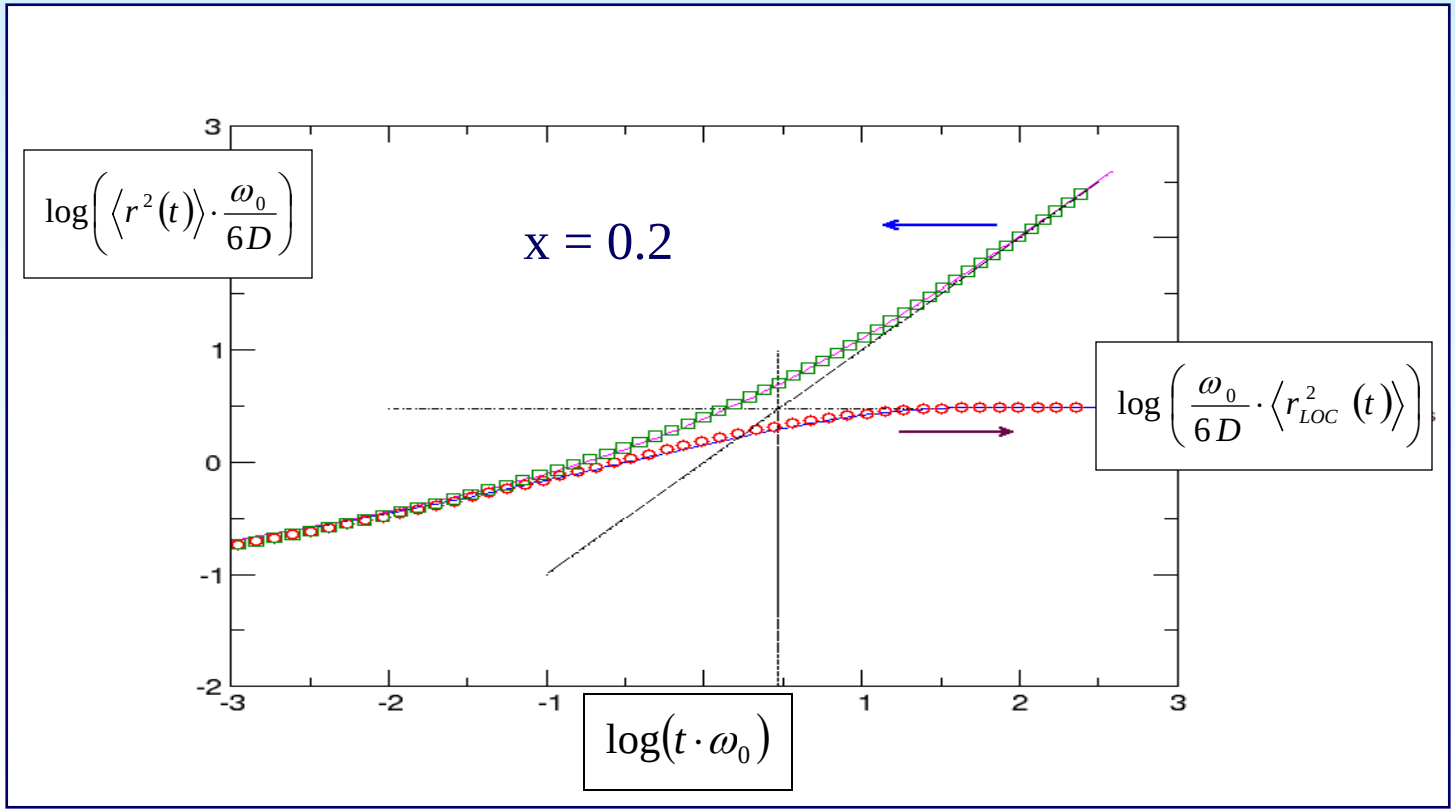
$$\varepsilon_S(\omega_S) = \frac{\omega_0 \cdot \varepsilon_0 \cdot (\varepsilon(\omega_S) - \varepsilon(\infty))}{\sigma(0)} = \frac{1}{\omega_S} \cdot \mathrm{Im}\,\hat{\sigma}_S(\omega_S)$$



Localized mean square displacement for glasses x Na_2O (1-x) GeO_2

$$\left\langle r_{LOC}^2(t)\right\rangle = \left\langle r^2(t)\right\rangle - 6Dt = 6D\cdot\int_0^t (W_S(t')-1)dt'$$

Therefore: $\varepsilon_S(\omega)\approx\frac{\omega_0}{6D}\cdot FT\left[\frac{d}{dt}\left\langle r_{LOC}^2(t)\right\rangle\right]$ and $\varepsilon_S(0)=\frac{\omega_0}{6D}\left\langle r_{LOC}^2(\infty)\right\rangle$



$\left\langle r_{LOC}^2(\infty)\right\rangle^{0.5} \propto x^{-1/3}$ and about 65 % of average Na - Na distance

Treatment of localised motion:

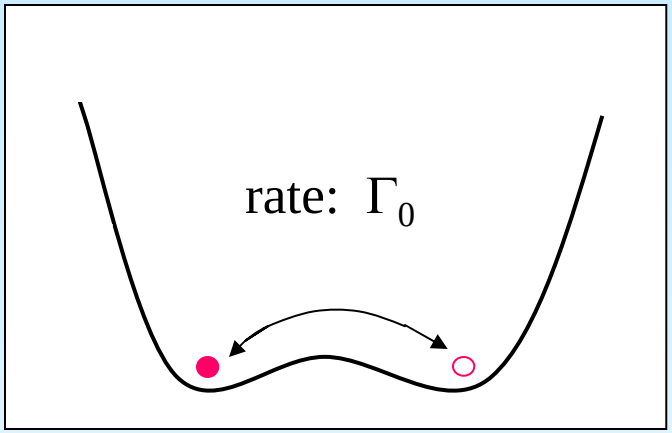
$$-\frac{\dot{W}_{NCL}(t)}{W_{NCL}(t)} = -B_{NCL} \cdot \dot{g}(t) + \Gamma_0$$

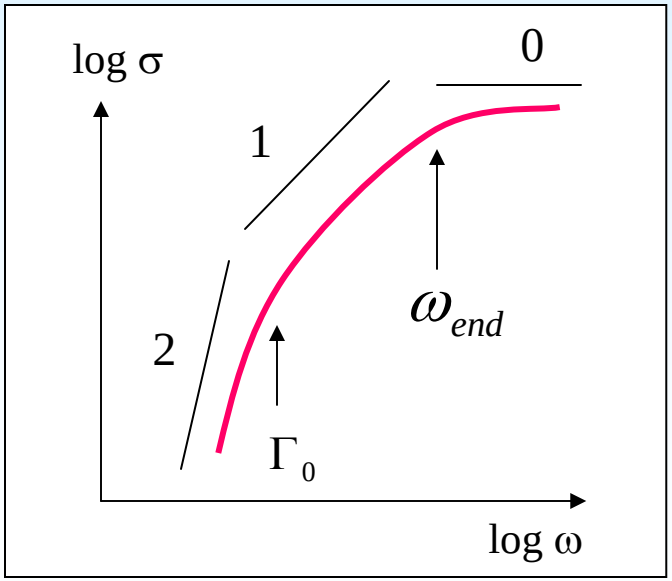
$$-\frac{\dot{g}(t)}{g(t)} = \text{.....}$$ as before, with $g(t)$ close to 1

$$W_{NCL}(t) = \frac{\Gamma_0}{(\omega_{end} + \Gamma_0)\exp(\Gamma_0 t) - \omega_{end}}$$

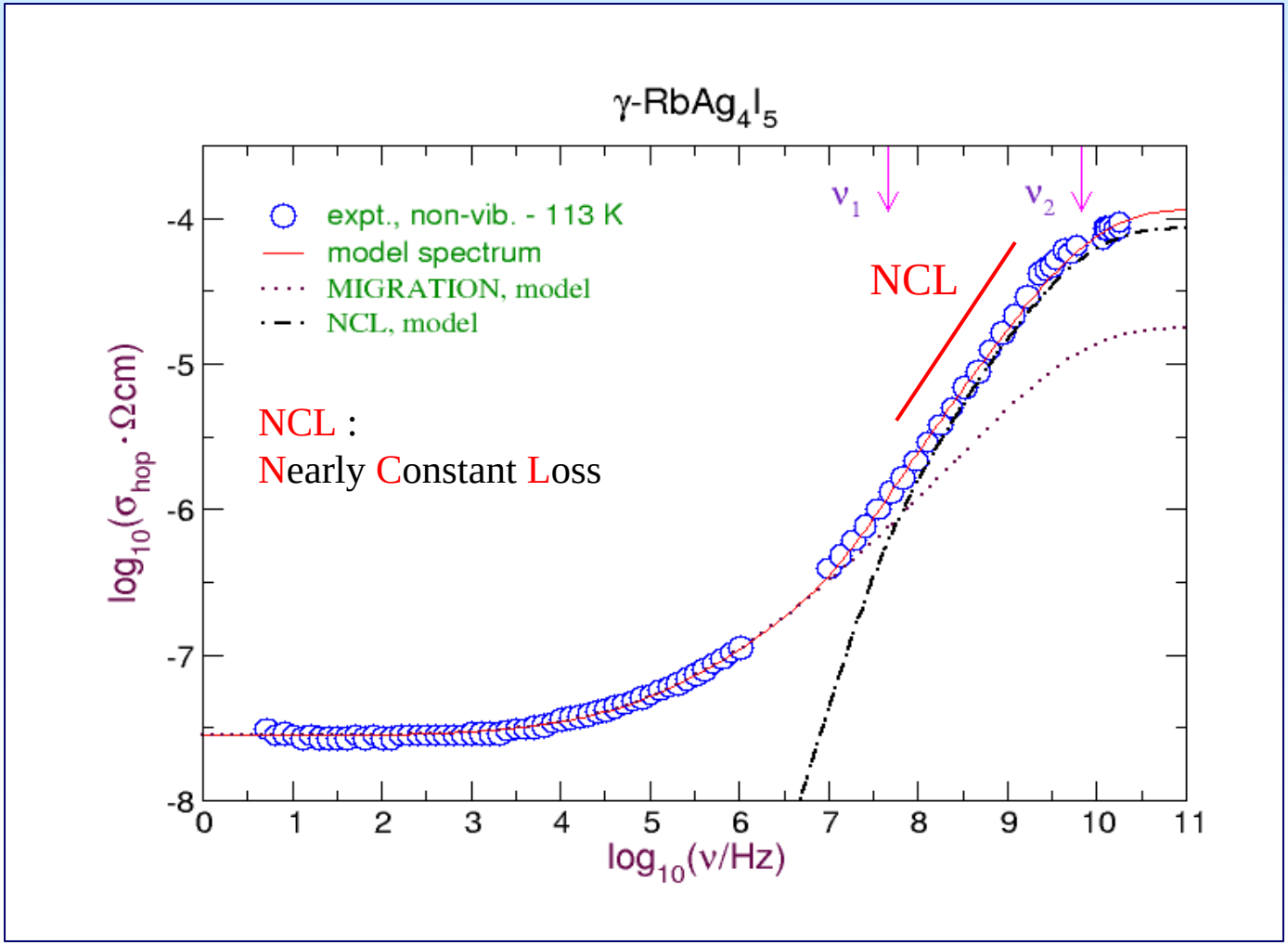
$$\omega_{end} = \Gamma_0 \cdot B_{NCL}^2$$

i.e., Debye for $B_{NCL} = 0$



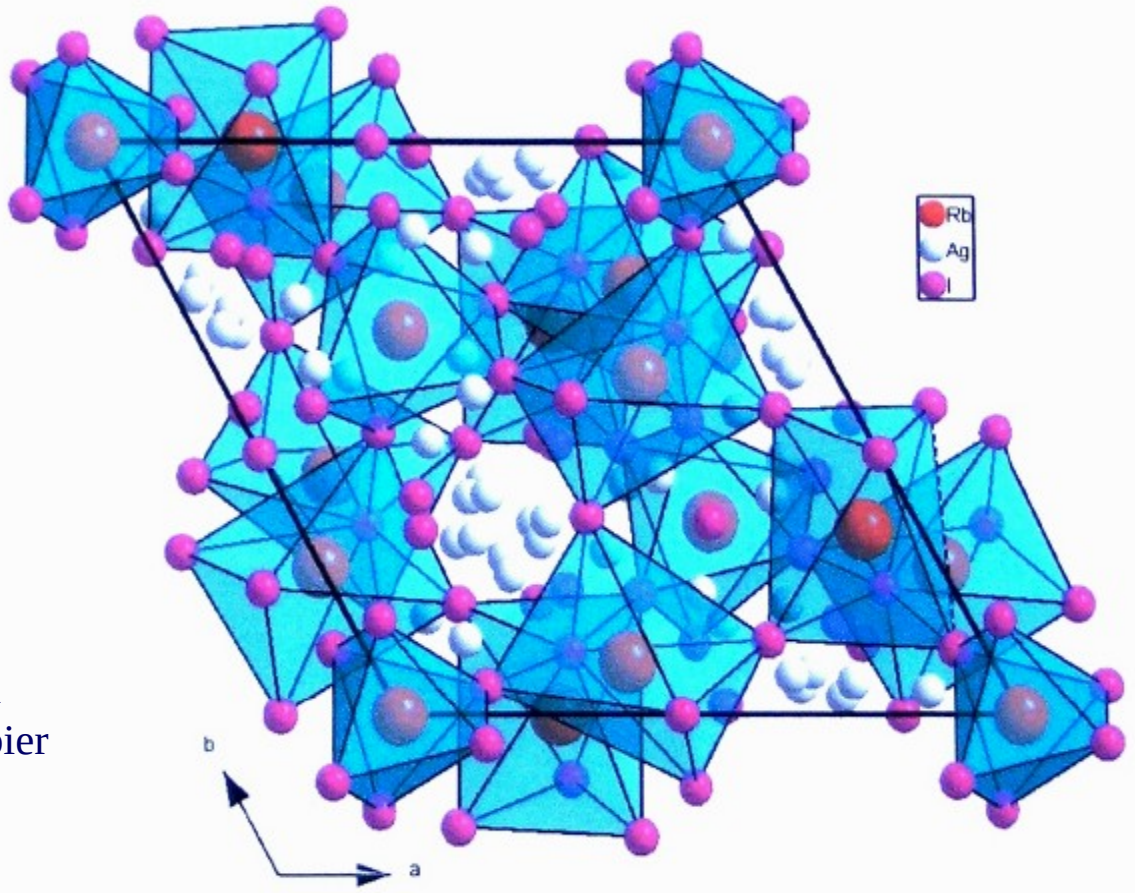


Conductivity spectrum of $RbAg_4I_5$, *below* the 121.8 K first order β–γ phase transition, after removal of the vibrational component



$\nu_1 = \Gamma_0/2\pi$ $\nu_2 = \omega_{end}/2\pi$

Structure of γ – Rb $Ag_4 I_5$



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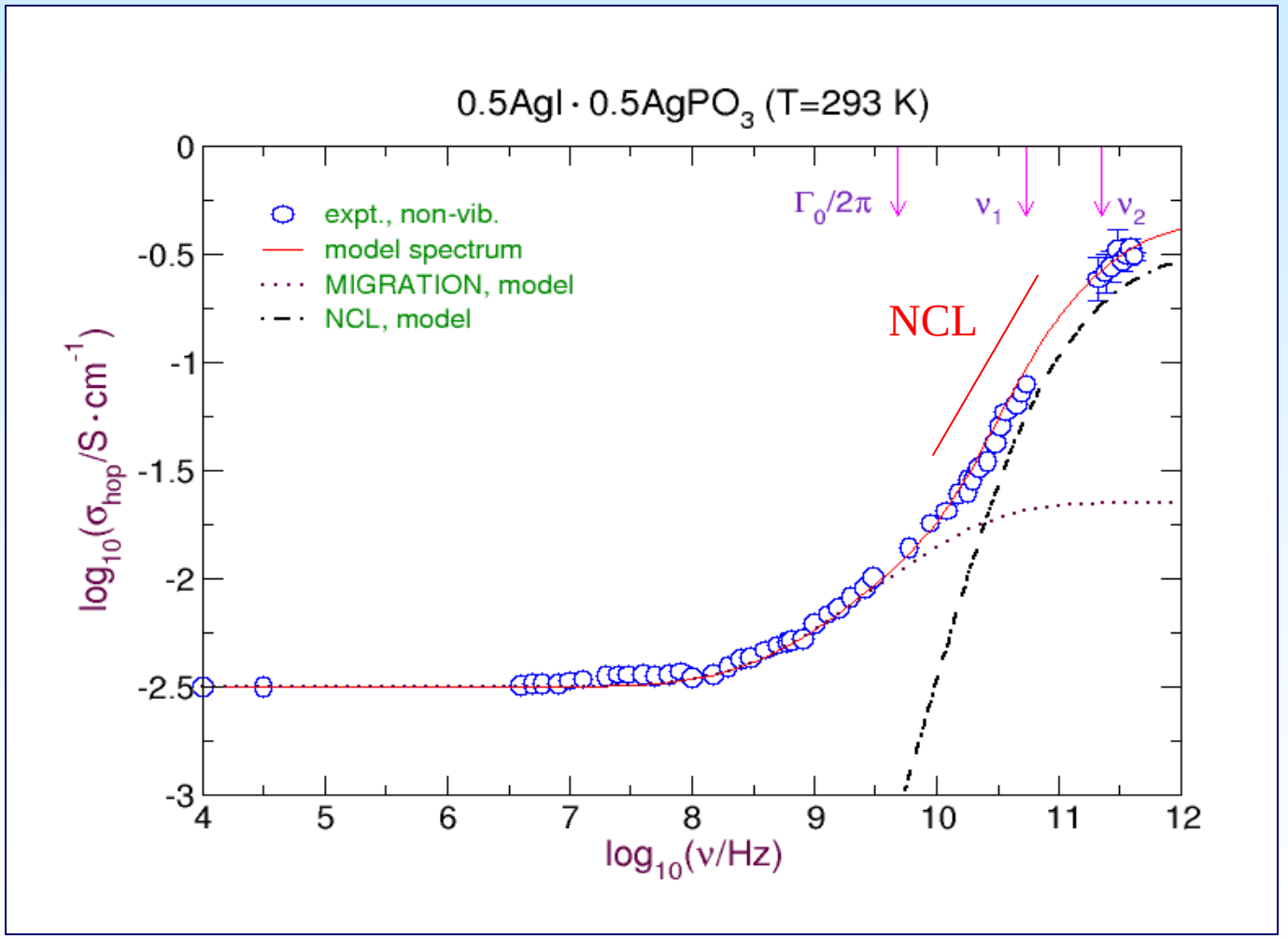
Conductivity spectrum of a silver iodide - silver metaphosphate glass, after removal of frequency-squared vibrational component



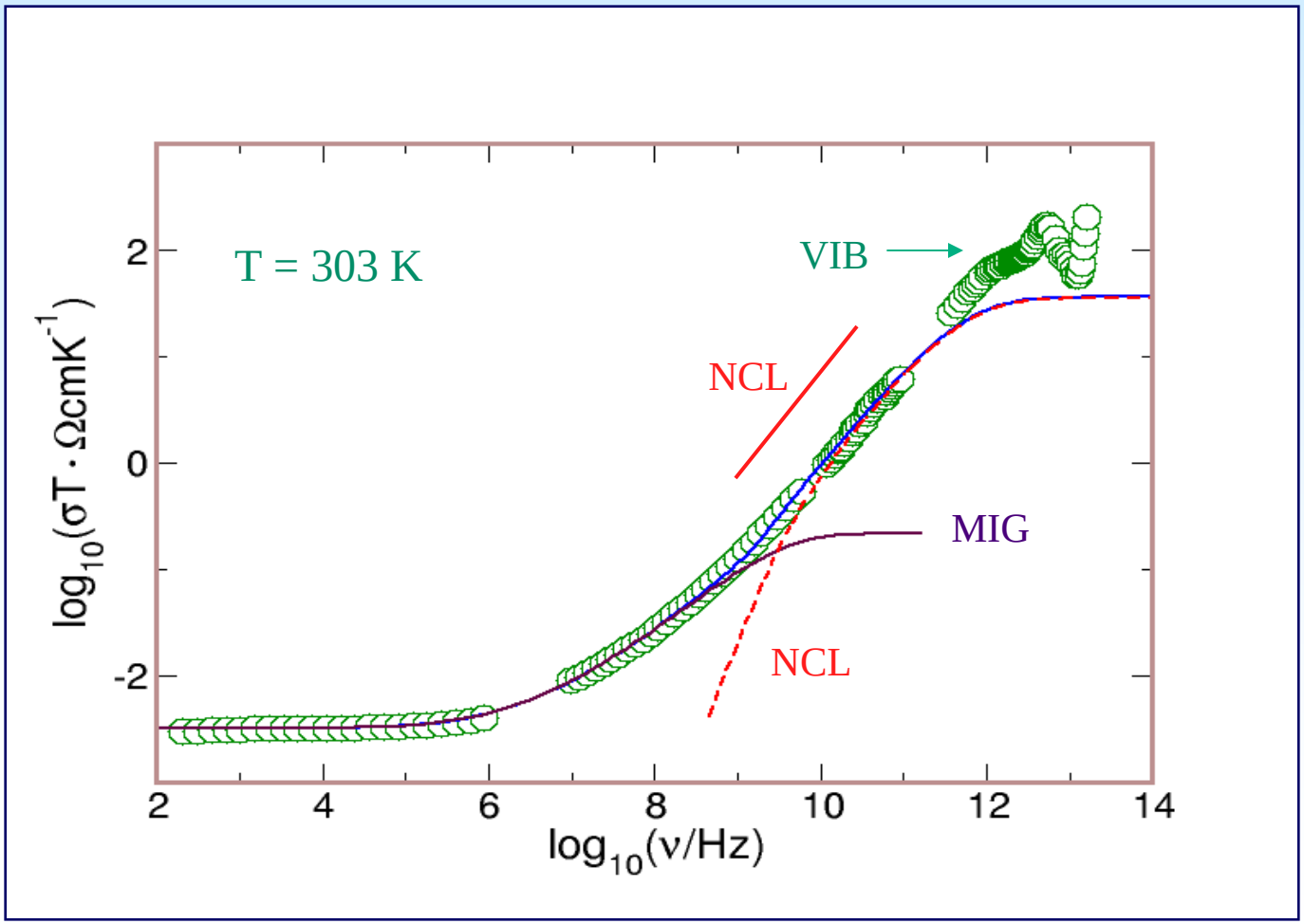
We now find : $\Gamma_0 / 2\pi << (\Gamma_0 / 2\pi)_{loc} = \nu_1$, ν_1 being activated with only 0.05 eV.

Localised motion is ubiquitous, e.g., Ag^+ - nBO^- dipoles

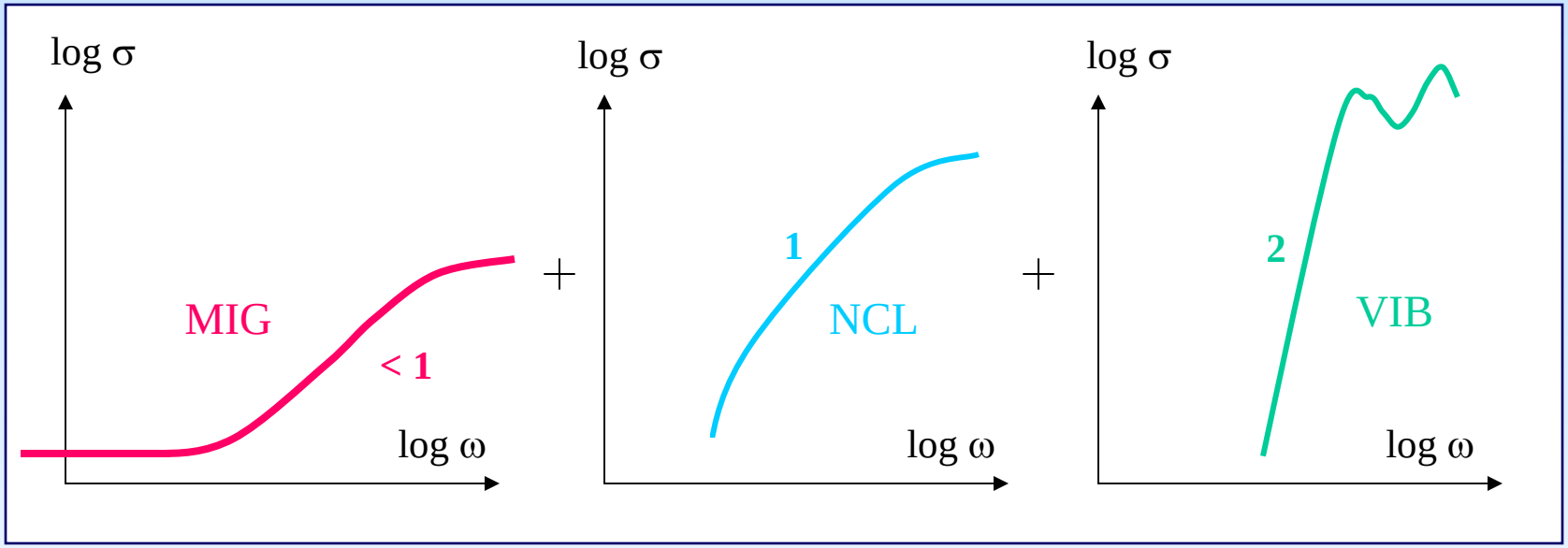
Conductivity spectrum of $NaPF_6$ (1 molal) in a polyurethane,

prepared by crosslinking a tri-functional random PEO : PPO copolymer,

4 : 1 by mol, M_W ~ 3600 g / mol



Conclusion



Ionic materials with disordered structures
(crystalline, glassy, polymeric)
always show this kind of superposition
caused by

potentially translational hopping motion

strictly localised non-vib. motion

vibrational motion

all three of them being collective and cooperative in character.

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