IMI-NFG's MITT Course on
Relaxation Processes in Glass

Electrical Relaxation

Topic 3: Nearly constant loss – second universality

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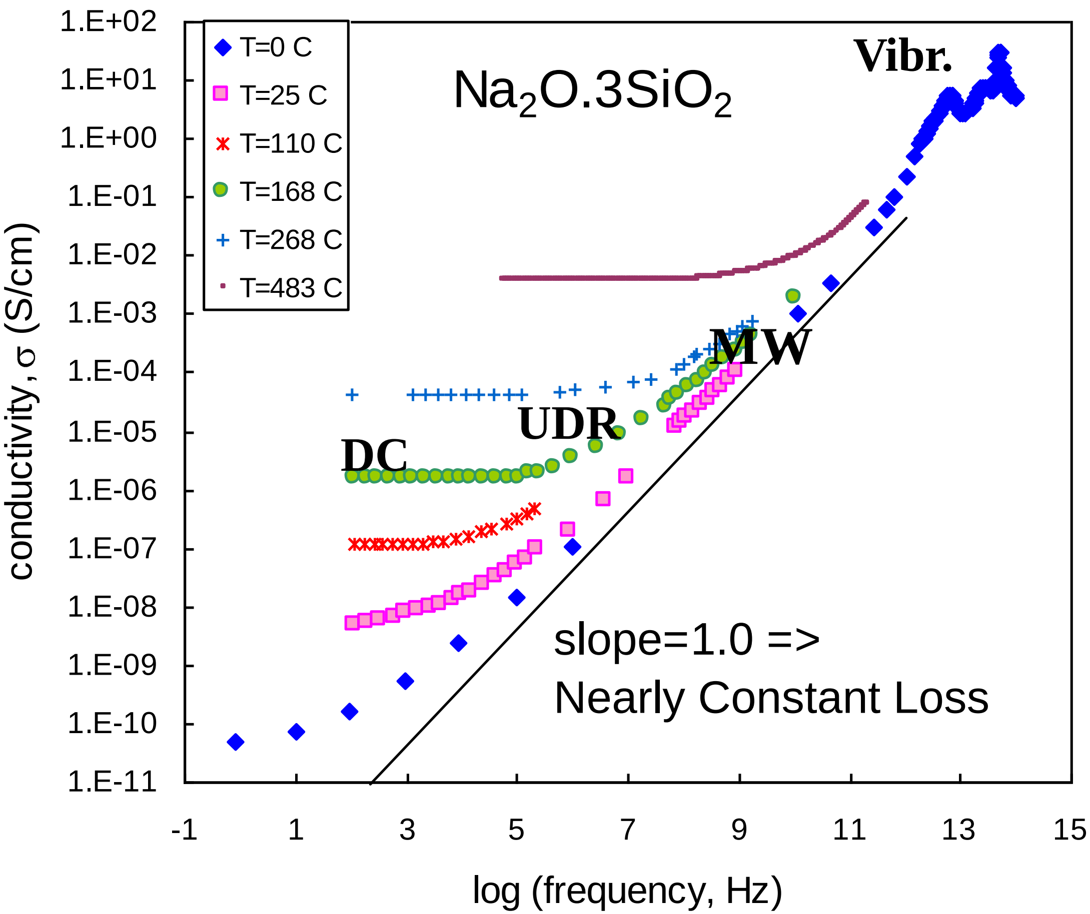
Outline: Electrical relaxation

1. Introduction – what is electrical about it?
2. Basics of electrical and dielectric relaxation
3. Data representations
4. BNN relation
5. Universal dielectric response
6. **Nearly constant loss – second universality**

Resources

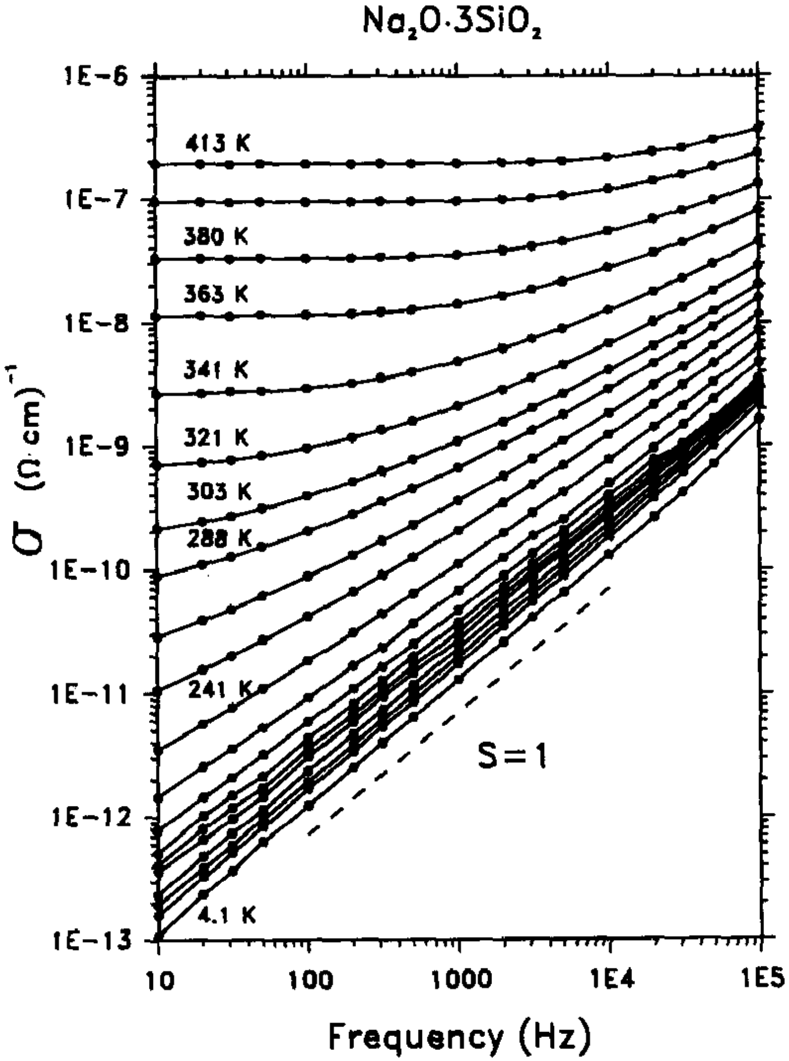
- 'Jellyfish' Atom Movement in Inorganic Glasses, H. Jain, Met. Mater. Process. 11, 317 (1999)
- Properties of the constant loss in ionically conducting glasses, melts, and crystals, KL Ngai, J. Chem. Phys. 110, 10576 (1999)
- 'Jellyfish' fluctuations of atoms in solids, H. Jain, S. Krishnaswami, O. Kanert, J. Non-cryst Solids 307-310, 1017 (2002)

Regimes of Ion Conduction in Common Glasses



Data from Burns et al. *Phys. Chem. Glasses*, 30,1989, 264.

Low-f Conductivity over a wide T range



$\sigma \sim \omega^s$

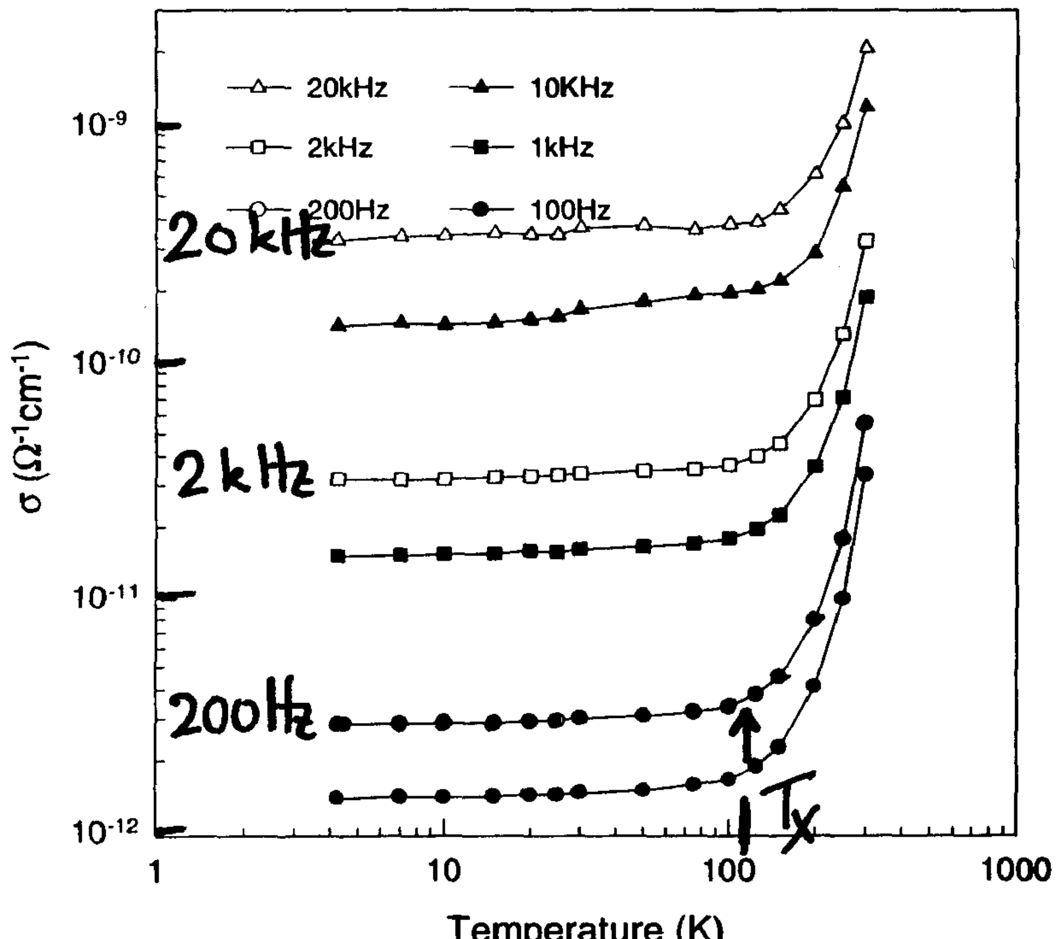
$s \sim 1 \Rightarrow$ nearly constant loss

Nowick: second universality

Nowick et al. PRL (1991); Lu and Jain, J. Phys. Chem. Solids 55 (1994)
Also, Sidebottom et al., PRL (1995); Moynihan, JNC S (1994); Ribes et al. (1996); etc .

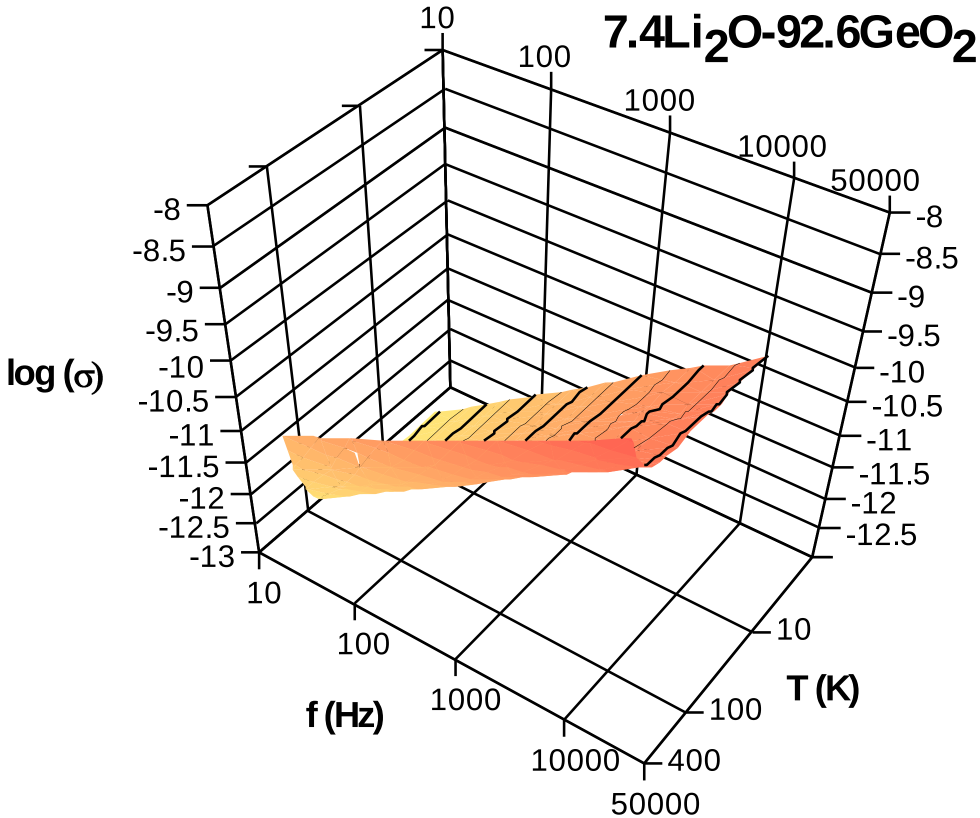
AC conductivity at low temperature: *T - dependence (4 K - RT)*

$0.074Li_2O: 0.926GeO_2$



Lu and Jain (1994)

σ-f-T Plot



The clear delineation of the 3-D σ-f-T plots into two surfaces => Two independent phenomena.

In most cases........

Empirically,

Low f, high T

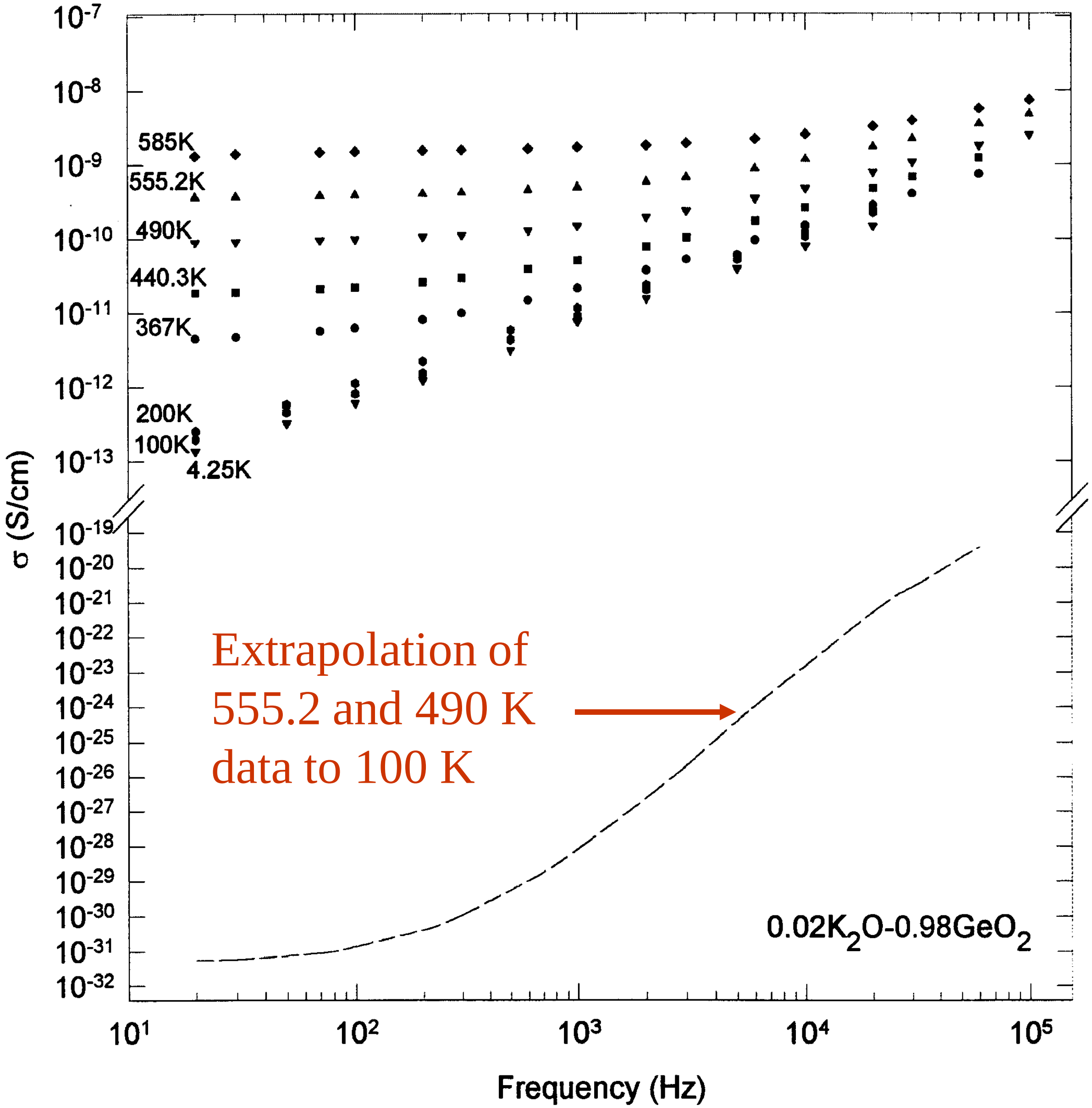
Intermediate f, high T

Intermediate f, low T

$$\sigma T\ (\omega, T) = A \exp(-E_{dc}/kT) + C_1\, \omega^s \exp(-E_{ac}/kT) + \boxed{C_2 \omega^{\beta}\, T^{\,1+\alpha}}$$

where $0<s<1$, typically 0.6; $0<\alpha<0.25$; $1.0<\beta<1.25$

Diffusive conductivity at low T?

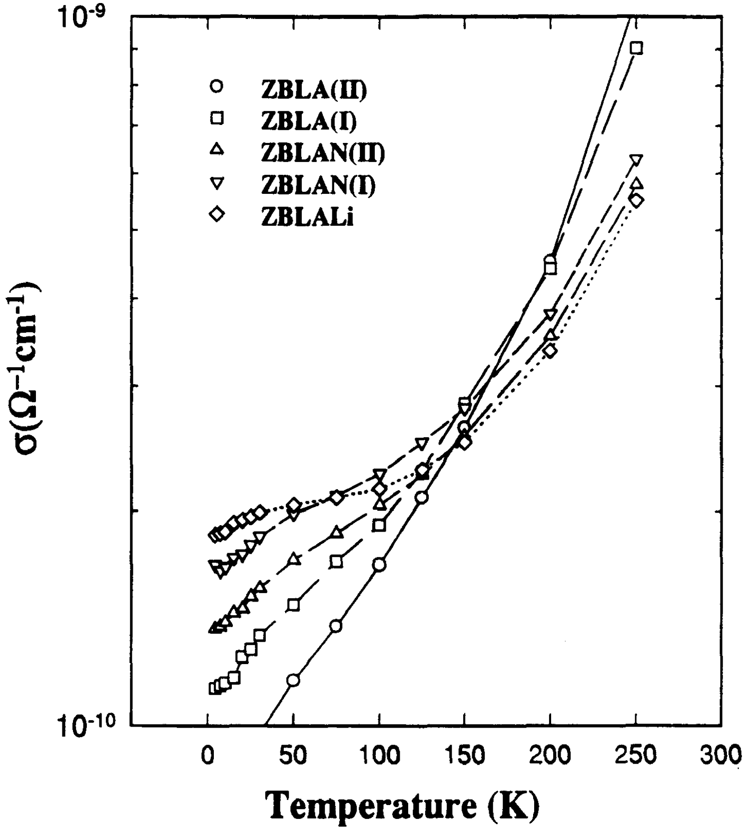


A thermally activated single atom diffusive motion is all frozen at low-T

=>

It is not possible to observe any diffusive conduction at low T.

AC conductivity at low T: Heavy metal fluoride glasses

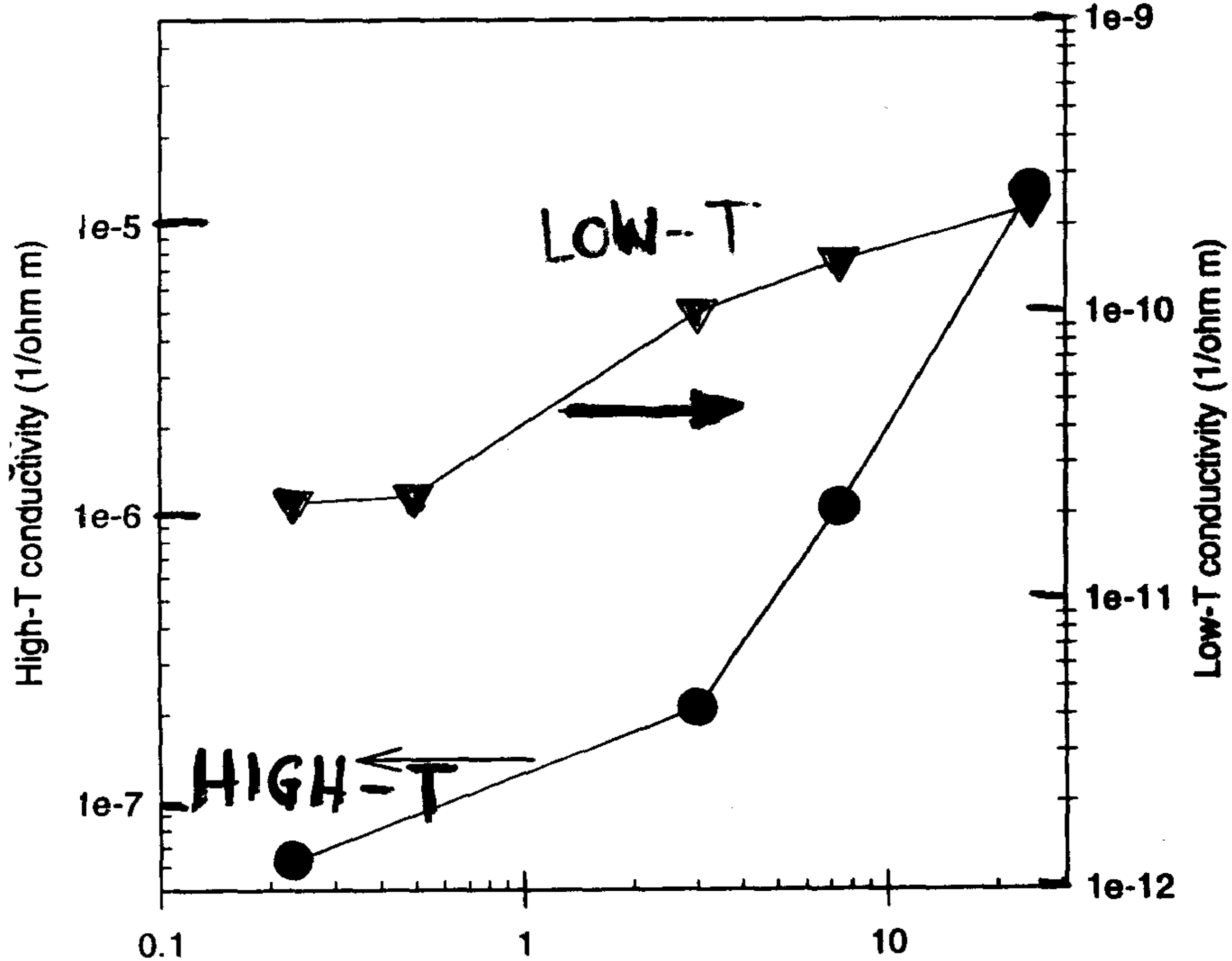


Small changes in composition affect the low-T and high-T σ very differently. So the two σ's should have different origins.

Glass	ZrF4	HfF4	BaF4	LaF3	AlF3	LiF	NaF
ZBLALi	48.22	---	22.41	4.64	3.54	21.19	---
ZBLAN(I)	54.82	---	25.00	4.04	3.16	---	13.52
ZBLAN(II)	27.40	27.40	19.76	3.06	3.19	---	19.19
ZBLA(I)	58.00	---	33.00	5.00	4.00	---	---
ZBLA(II)	59.45	---	30.87	5.69	3.99	---	---

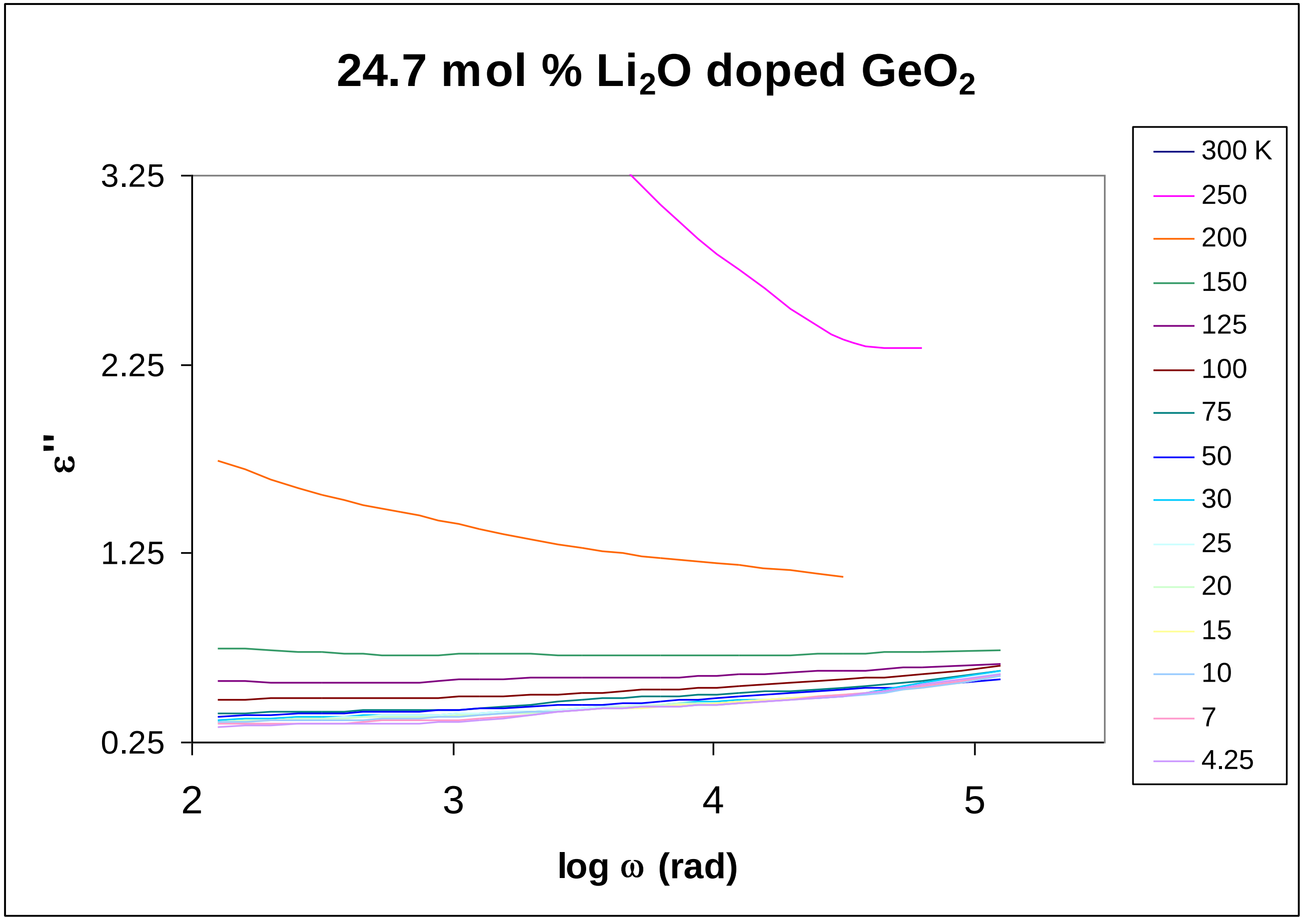
Mobile cation conc. dependence of σ

$xLi_2O:(1-x)GeO_2$



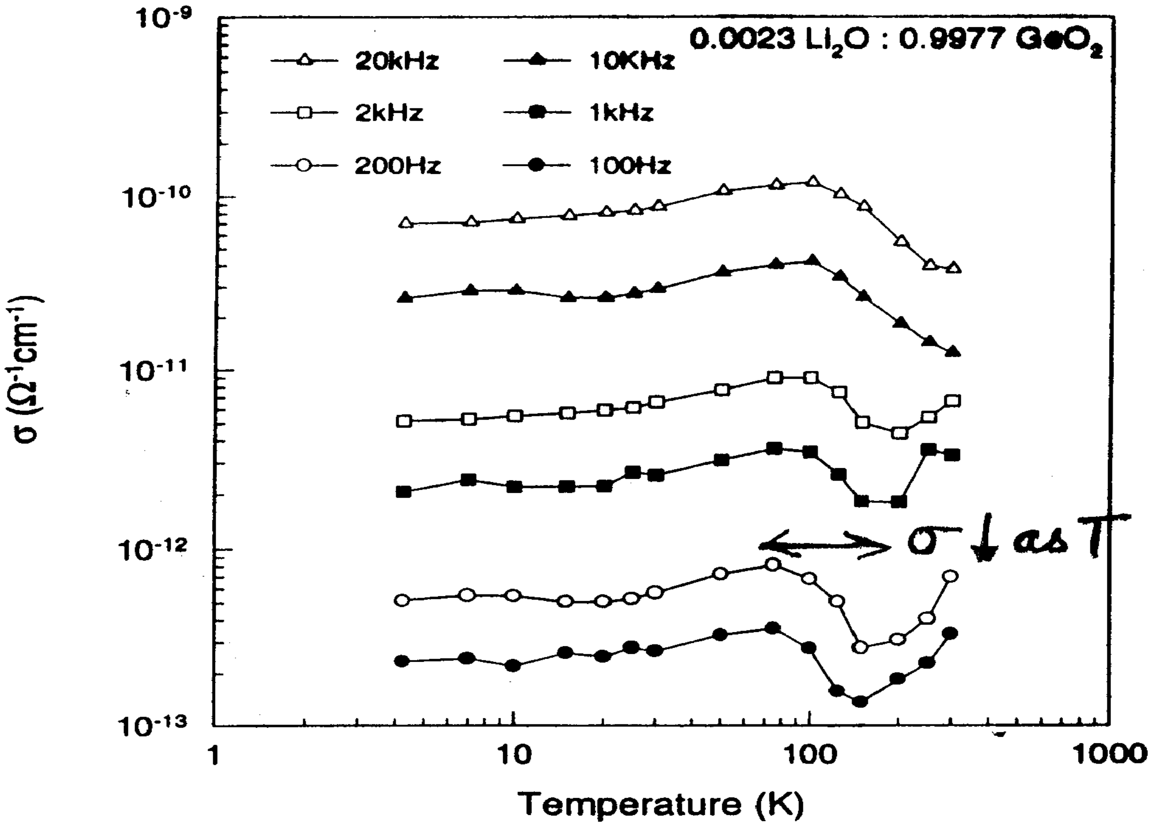
Even for a binary glass system the composition dependence of the high-T and low-T σ are very different.
High-T σ is much more sensitive to structure than low-T σ.

High x glass at low T: Only NCL is observed



Often s >1.0, which cannot be explained by the models of UDR

In a few cases, e.g. low alkali glass:

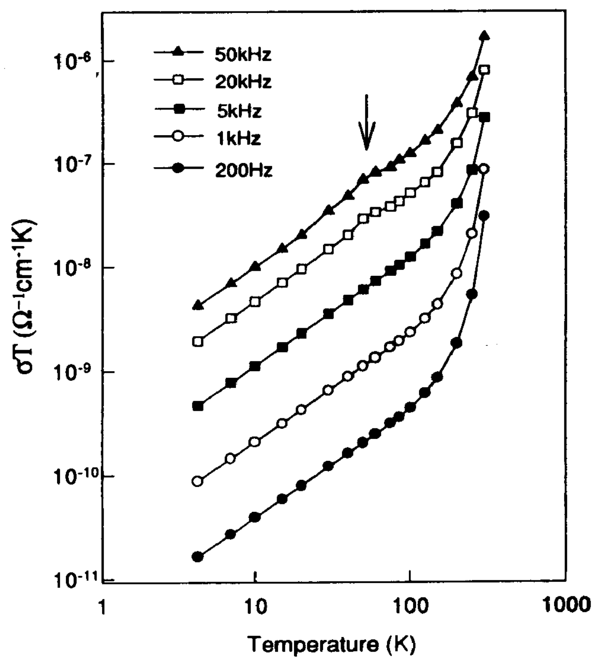


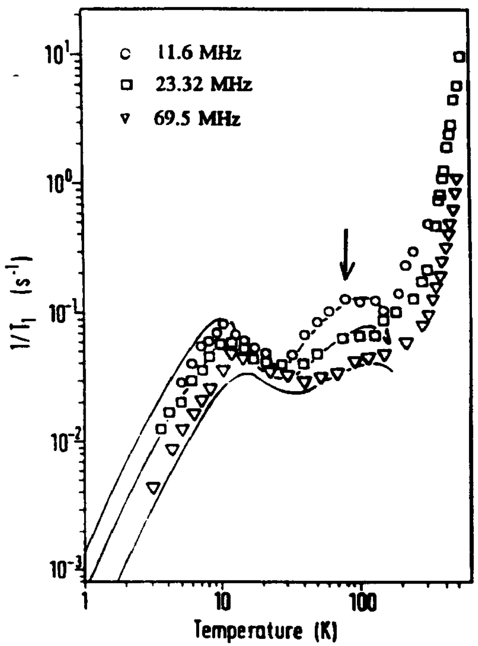
The maximum/minimum in σ(T) before the exponential increase cannot be understood by any high-T ion hopping mechanism.
NCL is superimposed with a discrete loss mechanism.

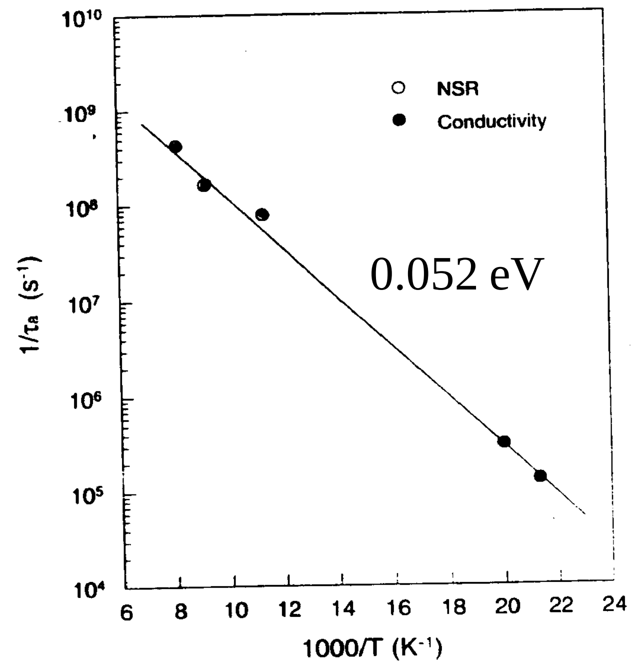
Lu & Jain, J. Phys. Chem. Solids (1994)

Comparison of NSR rate and σ at low T

Heavy Metal Fluoride Glass





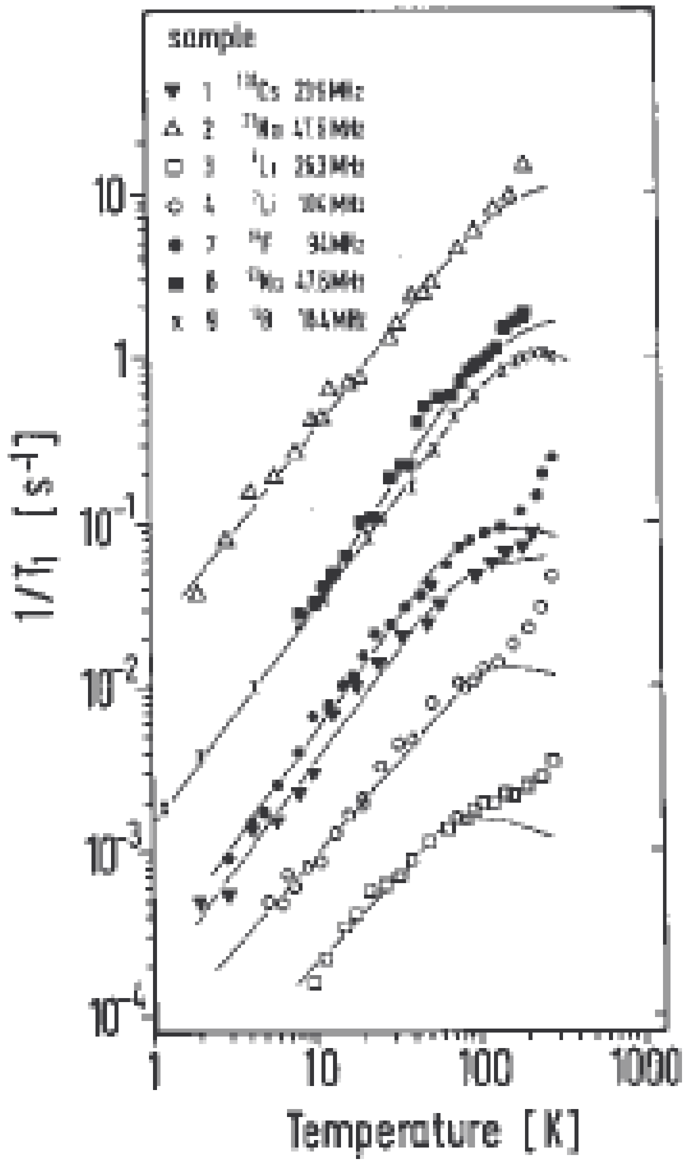


σ detects only one kind of jellyfish, but NSR may find more than one.

The pre-exponential factor is too low for single atom process⇒ A multi atom motion

Lu et al. Phil. Mag. 70 (1994)

Pre-historic observations of NCL

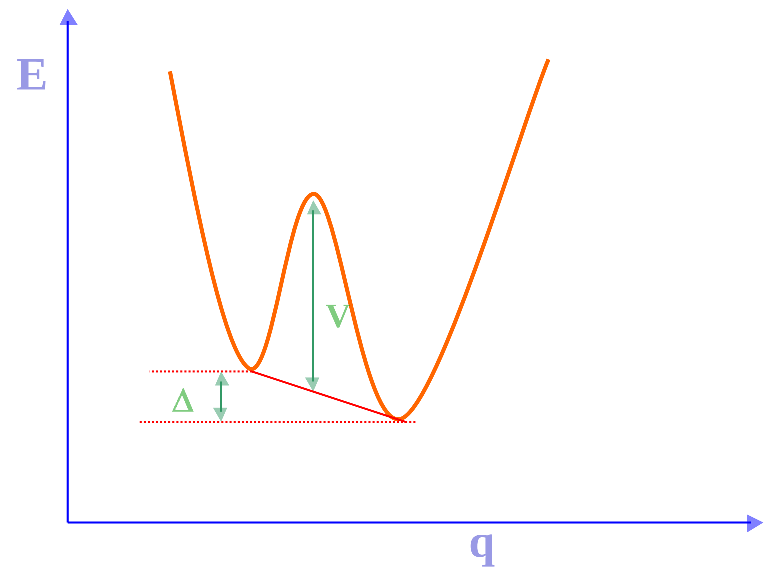


The temperature dependence of nuclear spin relaxation rate ($1/T_1$) at low temperatures follows power law which corresponds to nearly constant loss in electrical measurements.

Mueller-Warmuth, Eckert (1982)
G. Balzer-Joellenbeck, Kanert, Jain (1986)

Asymmetric Double Well Potential (ADWP) Model for low f - low T conductivity

- The jellyfish occupies one of (at least) two equilibrium positions of an asymmetric double-well potential.
- Under thermal activation, the atoms can move over the potential barrier in a *‘jellyfish-like’ wiggling motion.*
- There is a distribution of V and Δ due to structural disorder and ion-ion interactions.



V: Average potential energy barrier

Δ: Asymmetry energy.

V- Potential barrier height

Δ- Asymmetry energy

ADWP relations

$$\sigma(\omega,T) = \frac{\omega N e^2 R^2}{12kT} \int_0^{V_m}\int_0^{\Delta_m} \operatorname{sech}^2(\Delta/2kT)\,\phi(\Delta,V)\,\frac{\omega\tau}{1+(\omega\tau)^2}\,d\Delta\, dV$$

$$\phi(\Delta,V) = \frac{1}{\Delta_o V_o}\cdot \operatorname{sech}(V/V_o) \text{ and } \tau = \tau_o \cdot \operatorname{sech}(\Delta/2KT)\cdot \exp(V/KT)$$

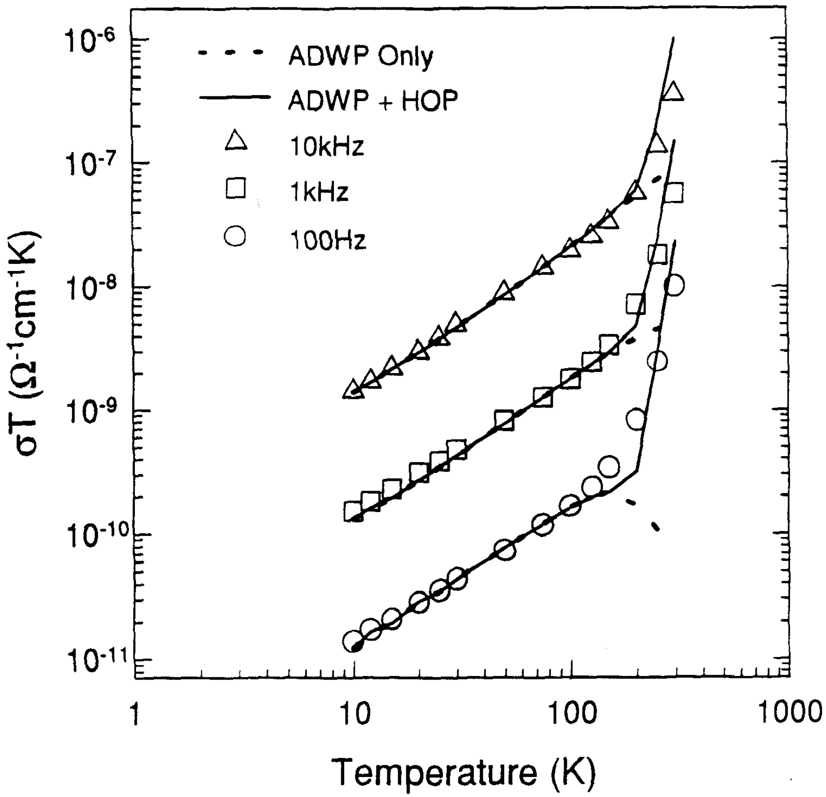
Approximations: At low T, (a) $kT \ll V_m$ (b) $V \gg kT$ and (c) $\Delta \gg kT$.

$$\boxed{\sigma(\omega,T) \sim N\, T^{\alpha}\, \omega^{\beta}}$$

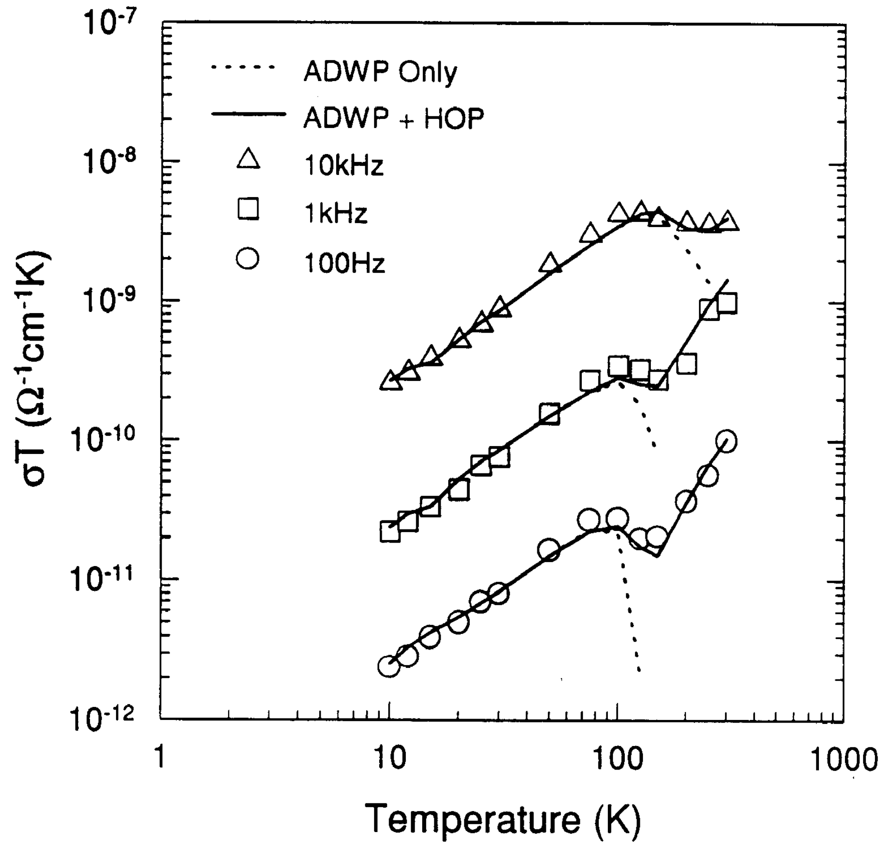
where α is determined by the maximum asymmetry of ADWP, Δ_{max}.
$\beta \sim 1+ (T/T_g)$

Comparison of the ADWPC model with exptl. data

$0.074\ Li_2O : 0.926\ GeO_2$



$0.0023\ Li_2O : 0.9977\ GeO_2$



Typical fitting parameters:

R=4 Å N≈3x10^{18} /cm^3

V_m=1000 K $\Delta_m=\Delta_o+\gamma T=3K+0.05T$

V_o=730 K $\tau_o=1\times10^{-6}$ sec

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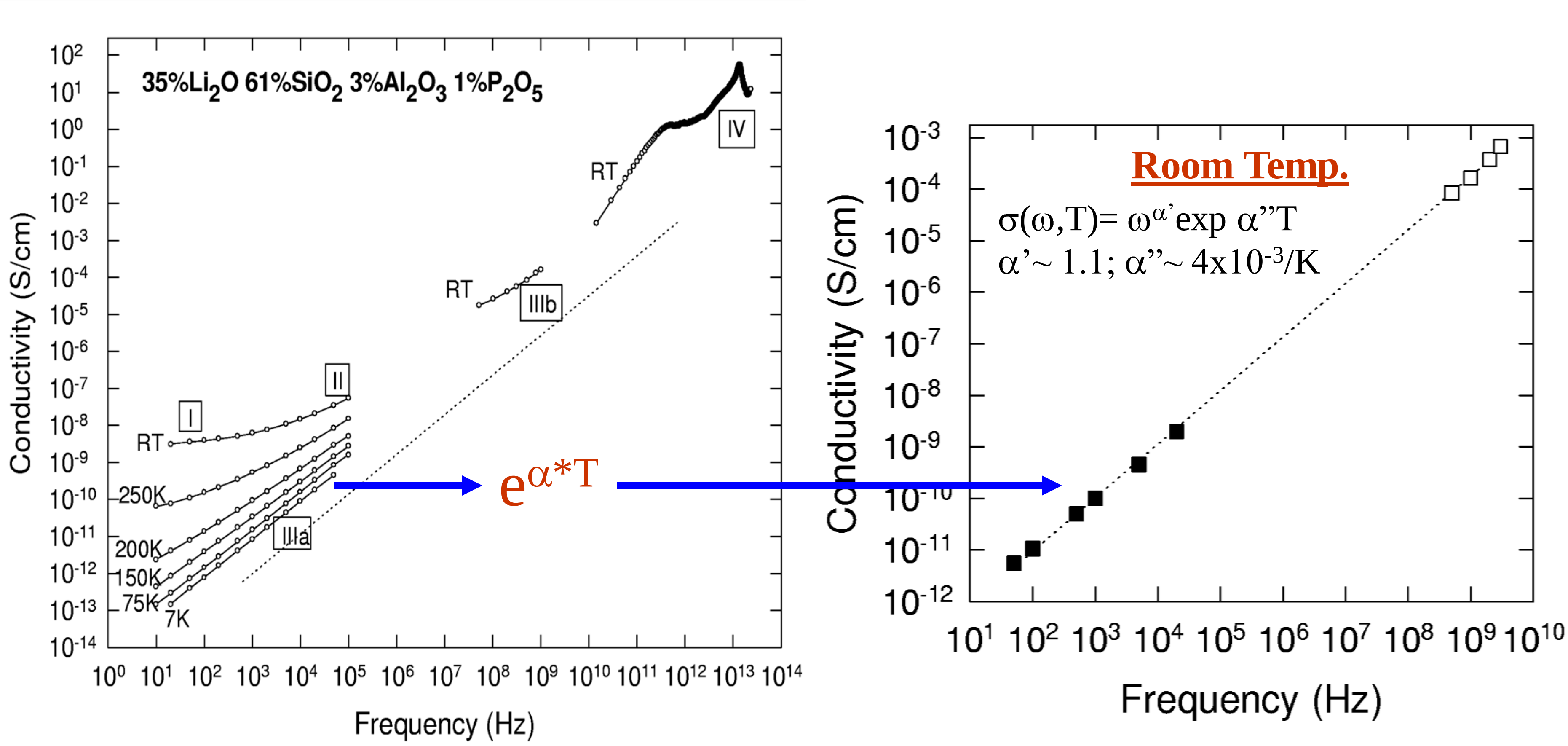
Connection between $\sigma_{low\ T\text{-}low\ \omega}$ (IIIa) and $\sigma_{RT\text{-}MW}$ (IIIb)



The source of conduction in these regions has a common underlying origin. (JNCS, 1996)

What is a jellyfish fluctuation?

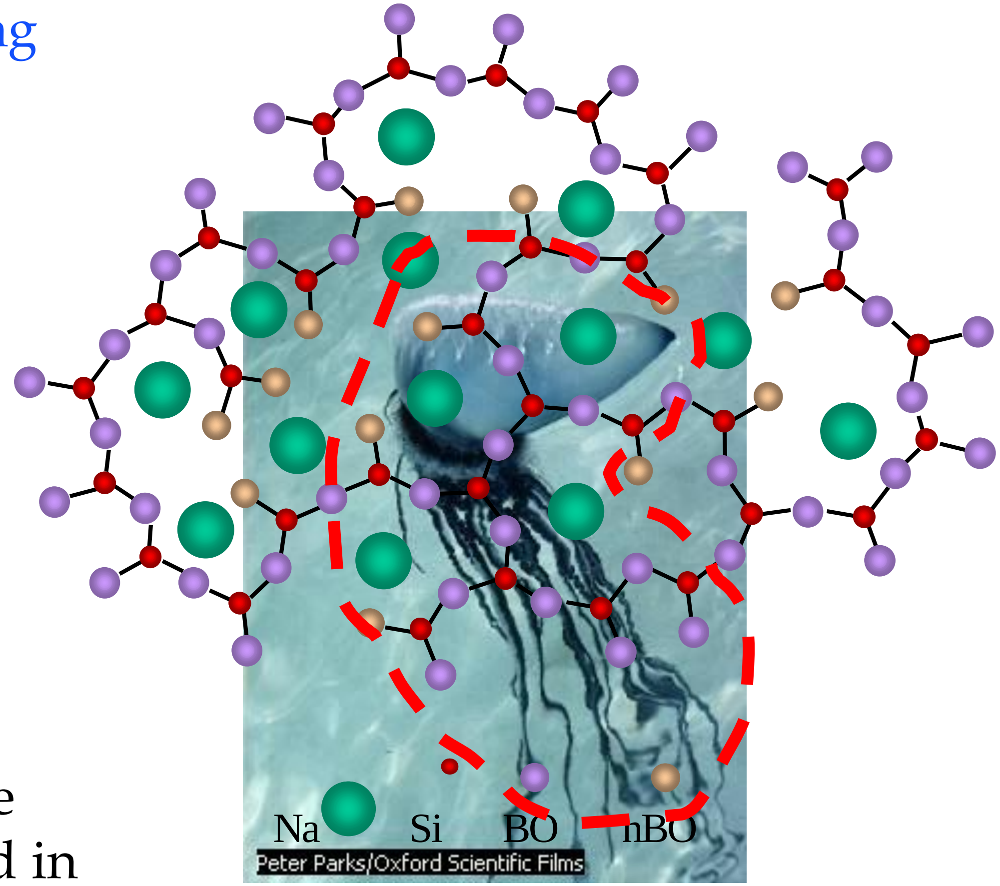
- It is a group of atoms which collectively move between different configurations, much like the wiggling of a ***jellyfish*** in ***glassy ocean***.

- There is no single atom hopping involved.

- The fluctuations are much slower than typical atom vibrations.

- The exact nature of the 'jellyfish' depends on the material.

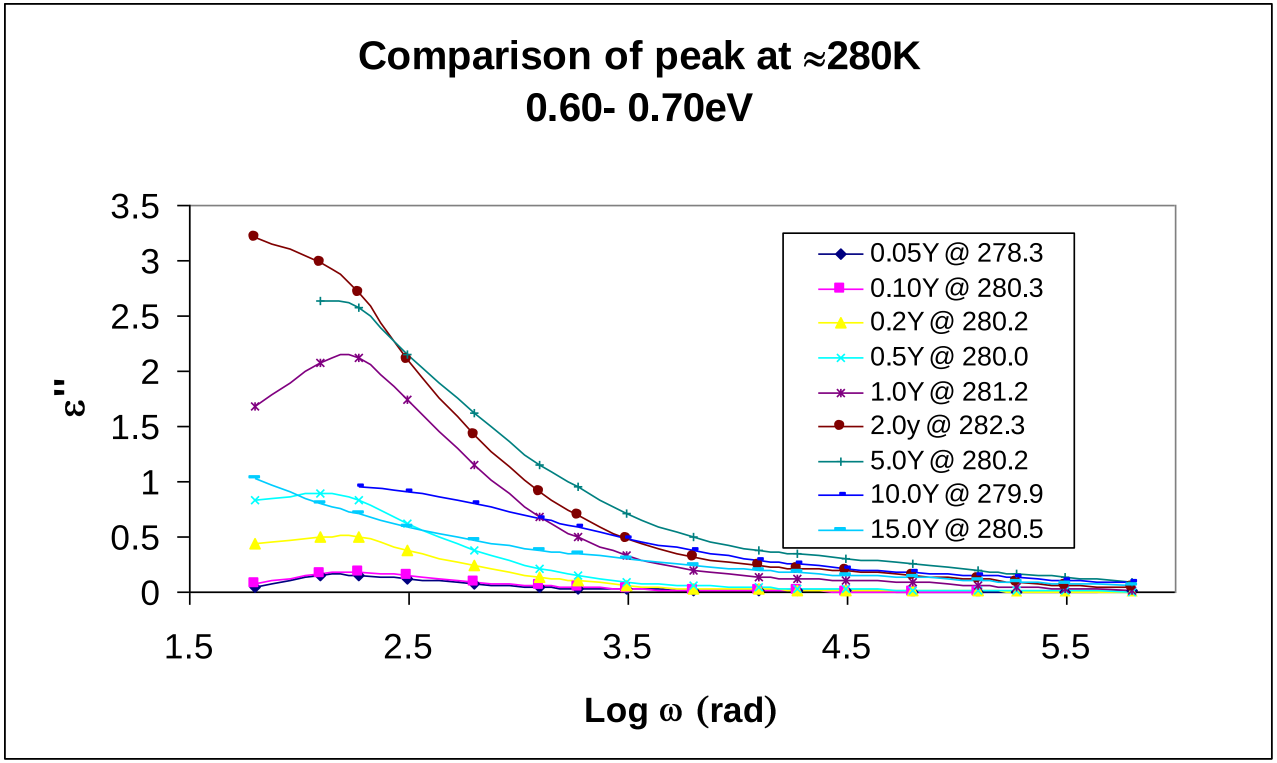
- In the same material more than one 'jellyfish' might exist and be observed in different T and f ranges.



ε″peak: well defined at low x, smearing at high x

Crystalline $xY_2O_3 – (1\text{-}x)CeO_2$

With increasing defect concentration, at first dipolar loss peak increases, then becomes lower in height and smears out as in NCL.



For the 280K peak, at $\omega = 10^{2.5}$ ε''_{max} ↑ for x: 0.05<0.1<0.2< 0.5≈15<10<1< 2≈5.

x_{max} = 2≈5 mol%

Laughman & Jain, unpublished

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Conclusions

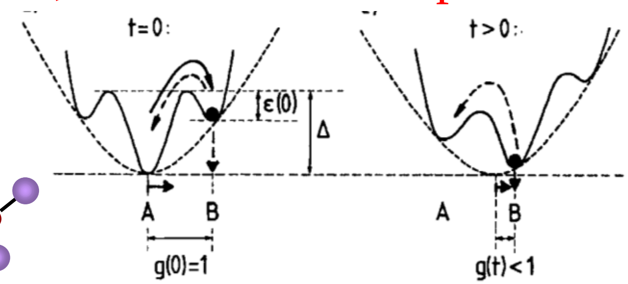
1. There exist **non-diffusive, non-vibrational, jellyfish fluctuations** that determine σ of common oxide glasses at *low T - low f*, and at *high T* - f_{MW} .

2. The NCL originates primarily from 'dipolar' fluctuations seen at low x clearly. The ADWPC model provides a good description of the observations for the non-diffusive movements in either region.

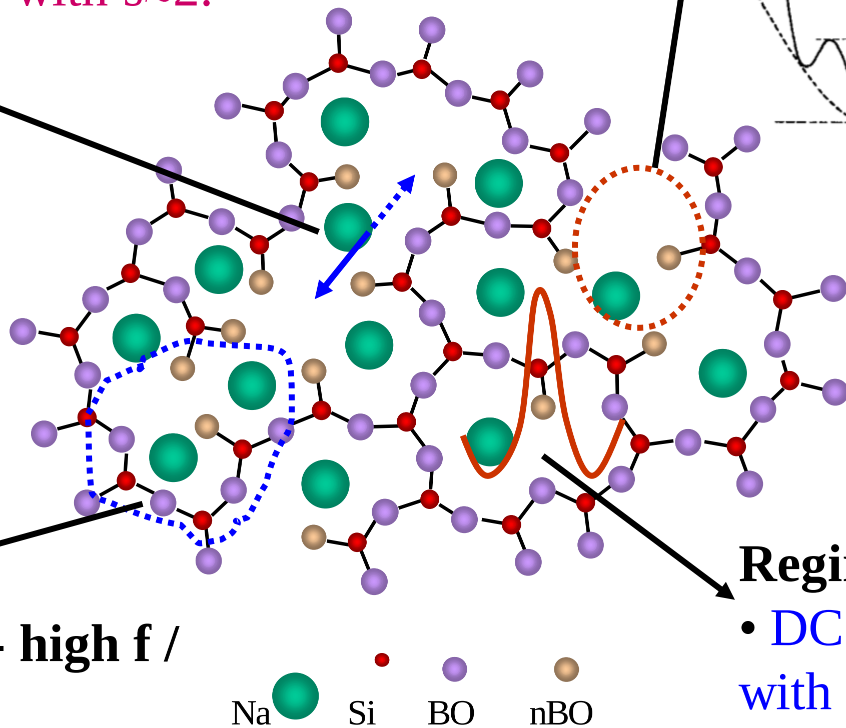
3. The 'jellyfish' are made of mobile as well as network atoms, the former being more important. The nature of jellyfish is modified when the mobile ions begin hopping.

Summary: A structural view of electrical relaxation

Regime II: High T - Intermediate f
- UDR region, with s≈0.6 and up.



Regime IV: Very high f
- Vibrational loss region, with s≈2.



Regime I: High T - low f
- DC conductivity region, with s=0.

Regime III: High T - high f / Low T - low f
- Jellyfish region, with s ~ 1.0.

Random network structure of a sodium silicate glass in two-dimension **(after Warren and Biscoe)**

Hope you had a chance to learn and feel relaxation!

Cheers!!