IMI-NFG's MITT Course on

Relaxation Processes in Glass

Electrical Relaxation

Topic 2: Universal dielectric response (UDR)

Himanshu Jain

Department of Materials Science & Engineering

Lehigh University, Bethlehem, PA 18015

H.Jain@Lehigh.edu

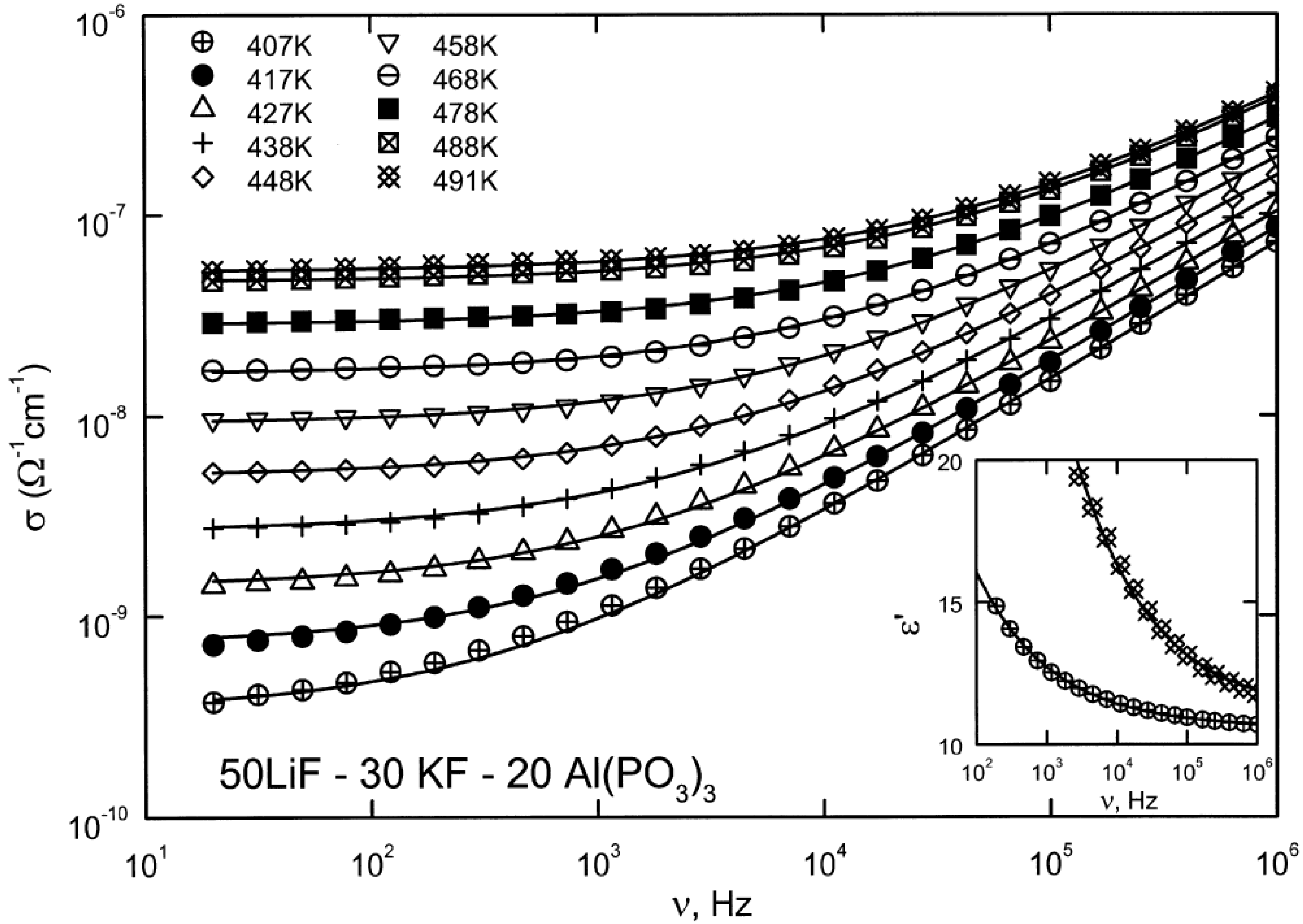
Outline: Electrical relaxation

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

- JC Dyre & TB Schrøder, 'Universality of ac conduction in disordered solids', Rev. Mod. Phys. 72, 873–892 (2000).
- JC Dyre, et al., 'Fundamental questions relating to ion conduction in disordered solids', Rep. Prog. Phys. 72 (2009) 046501.
- D. L. Sidebottom, 'Understanding ion motion in disordered solids from impedance spectroscopy scaling', Rev. Mod. Phys. 81 (2009) 999.
- Universal Relaxation Law, A.K. Jonscher, Chelsea Dielectric Press, London, 1996
- Impedance Spectroscopy – Theory, Experiment and Applications, E. Barsouvkov and J.R. Macdonald, Wiley 2005.

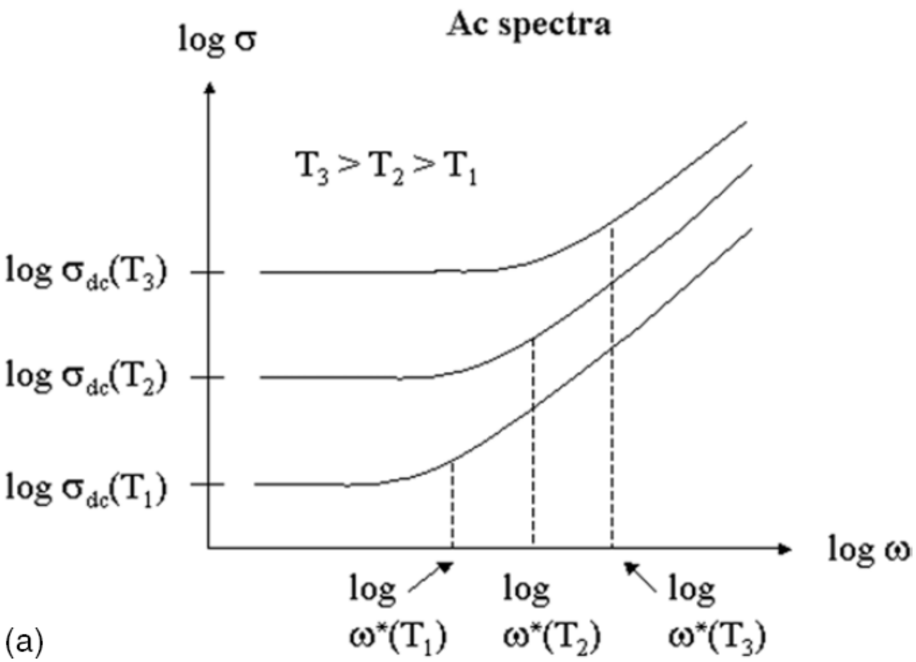
Low frequency conductivity dispersion

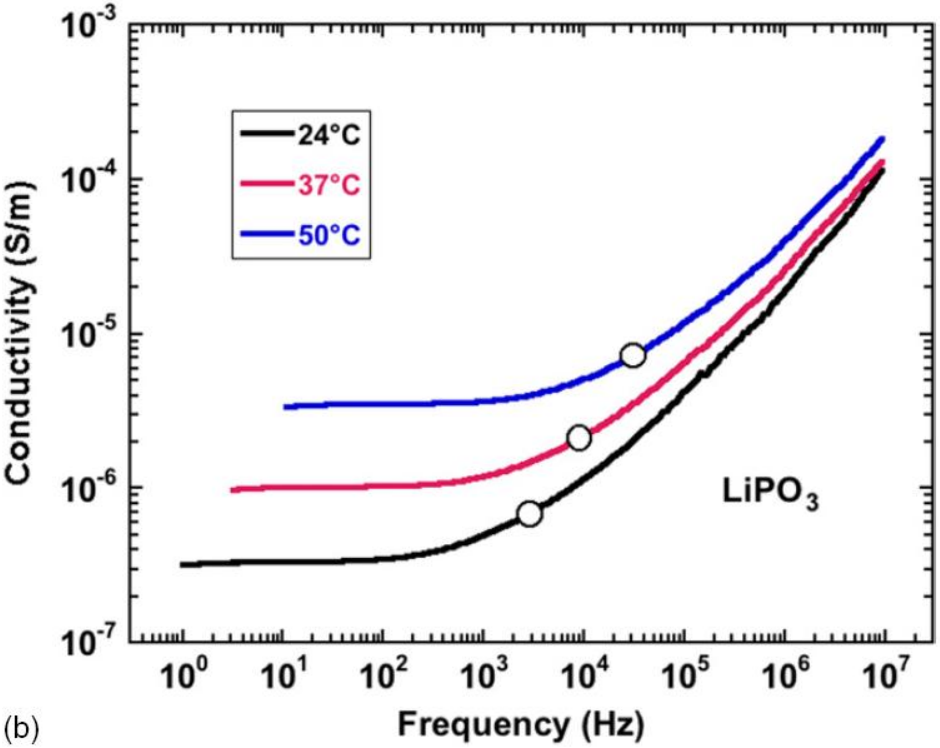


Conductivity continues to increase at ω > dielectric loss peak

Kulkarni et al., 1998, "Scaling behavior in the frequency dependent conductivity of mixed alkali glasses," Solid St. Ionics **112, 69–74.**

ω and T dependence of σ





Schematic figure showing the real part of the ac conductivity as a function of frequency at three different temperatures. As temperature is lowered, the dc conductivity decreases rapidly. At the same time the frequency marking the onset of ac conduction also increases (in proportion to the dc conductivity). (*b) The real part of the ac conductivity at three* different temperatures for a lithium-phosphate glass. The circles mark the frequency for onset of ac conduction. Dyre et al. (2009)

Universal Dielectric Response

Jonscher (1977): Empirical law approximately obeyed by ionic glasses and many other unrelated materials

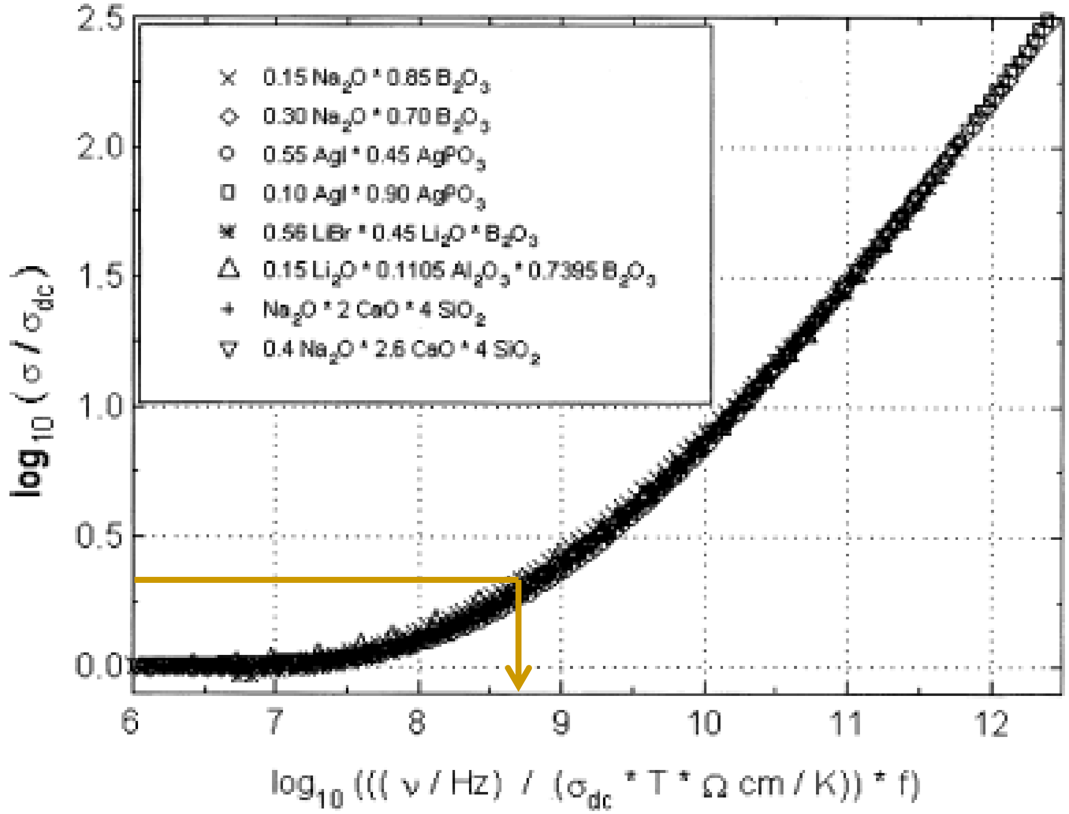
$$\sigma_{ac} = [\sigma_{dc} + (\omega/\omega_c)^n]$$

where n <1; ~0.6-0.8

•Some misfit, mostly near the bend. At higher freq n is insensitive to composition.

•ω_c is a characteristic frequency where $\sigma_{ac} = 2\sigma_{dc}$.

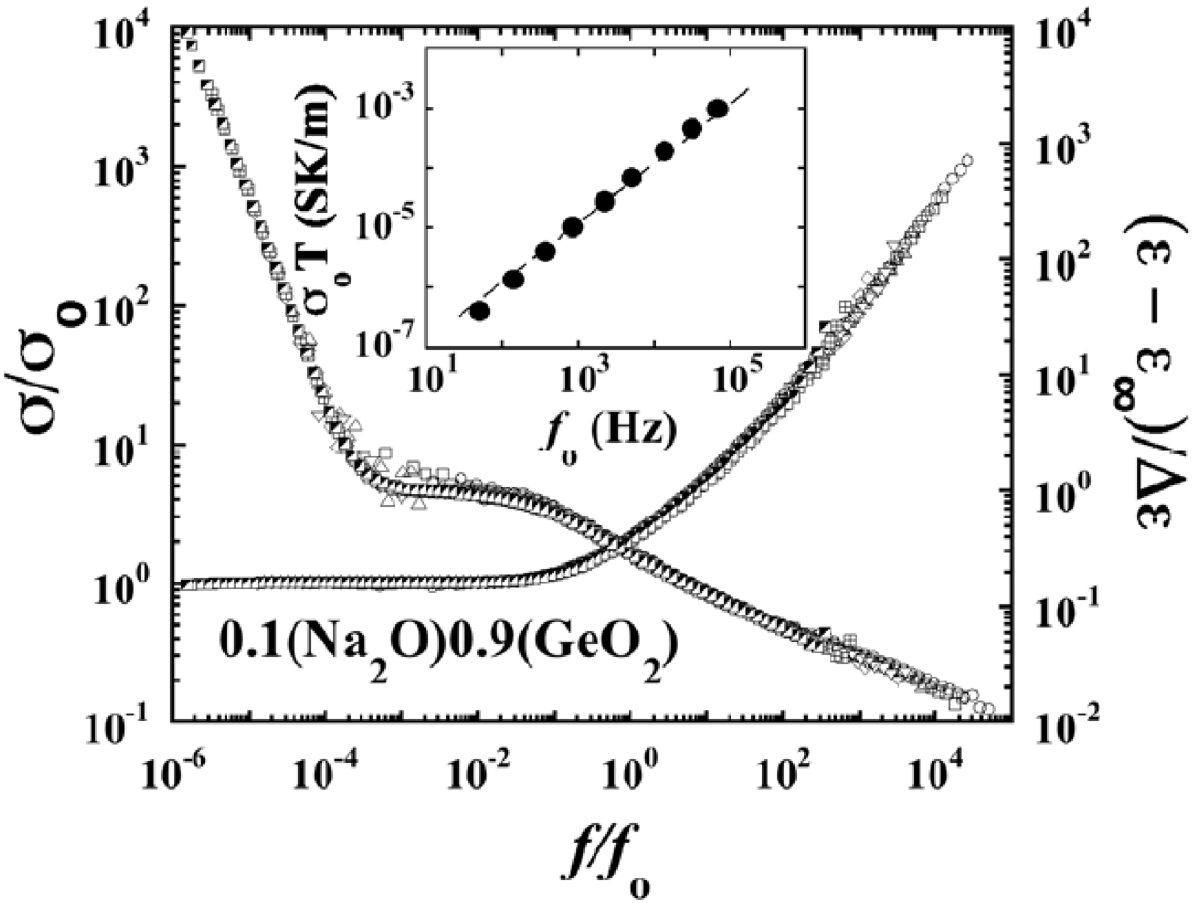
•Its identification as ion hopping frequency may not be valid.



Conductivity master curves of different glassy systems with scaling factor *f=mol% of* Na_2O *for the sodium borate glasses but a free scaling* parameter for the other glasses.

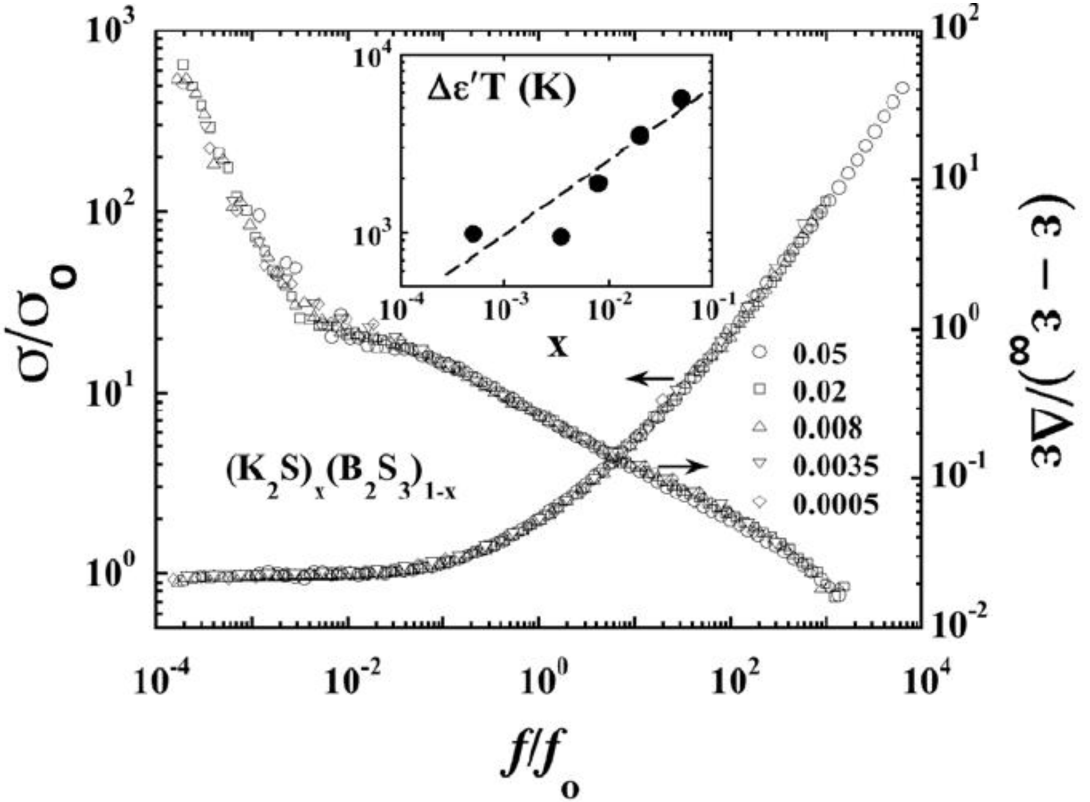
(Roling, Solid St. Ion. 1998)

Master plot with respect to temperature



D. Sidebottom, Rev. Mod. Phys. 2009, 81, 999

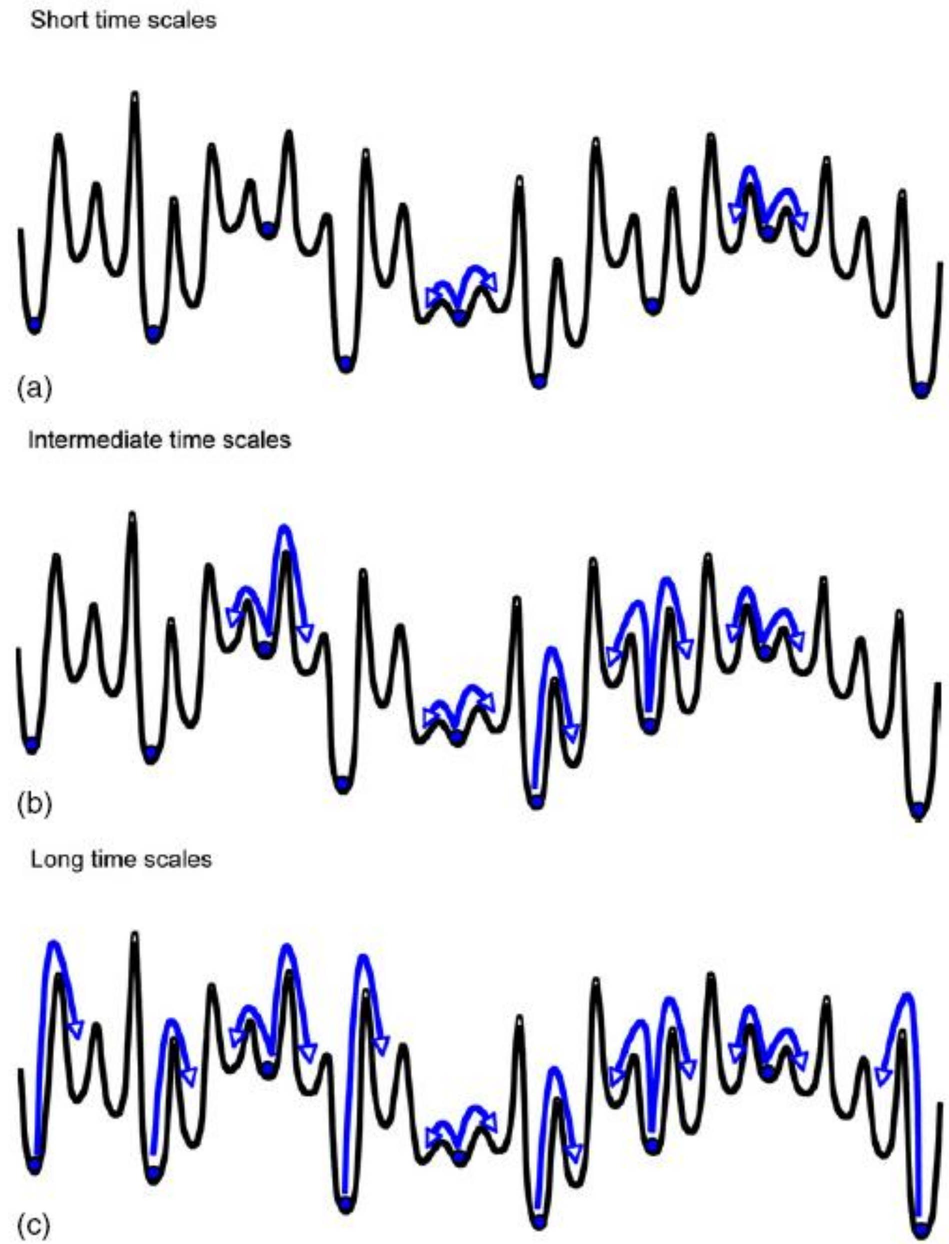
Master plot with respect to composition within a system



D. Sidebottom, Rev. Mod. Phys. 2009, 81, 999

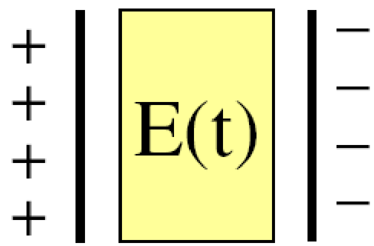
View of ion migration within its energy landscape

The arrows indicate attempted jumps. Most of these are unsuccessful and the ion ends back in the minimum it tried to leave: if the barrier is *E, according to rate* theory the probability of a successful jump is exp$(-E/k_BT)$
$\Rightarrow$ On short time scales only the smallest barriers are surmounted. As time passes, higher and higher barriers must be surmounted.

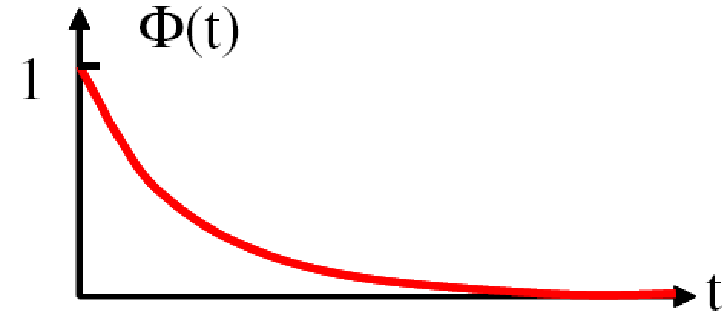


JC Dyre et al., 'Fundamental questions relating to ion conduction in disordered solids', Rep. Prog. Phys. 72 (2009) 046501.

Coupling model by Ngai (1979)



$$E(t) = \Phi(t)E(0)$$

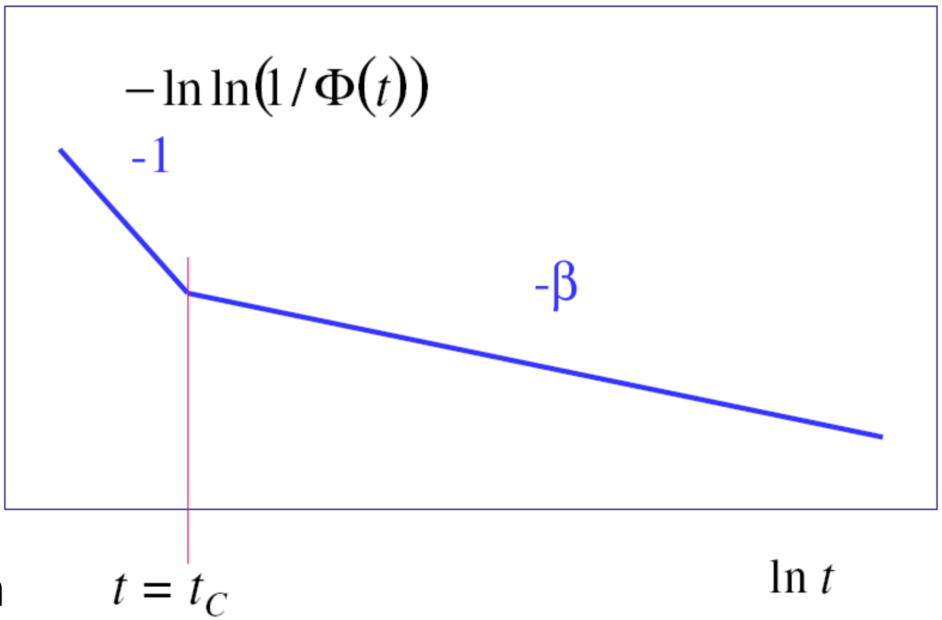


At very short time, $t<t_c$, primitive relaxing species are independent. Then: $\Phi(t) = \exp -(t/\tau_0)$.

After cross-over time t_c (T insensitive), they couple to the environment and slow down i.e.

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \quad 0 < \beta \leq 1.$$

Kohlrausch-Williams-Watts (KWW) function



Modulus formalism of UDR

Moynihan and Macedo (1974):

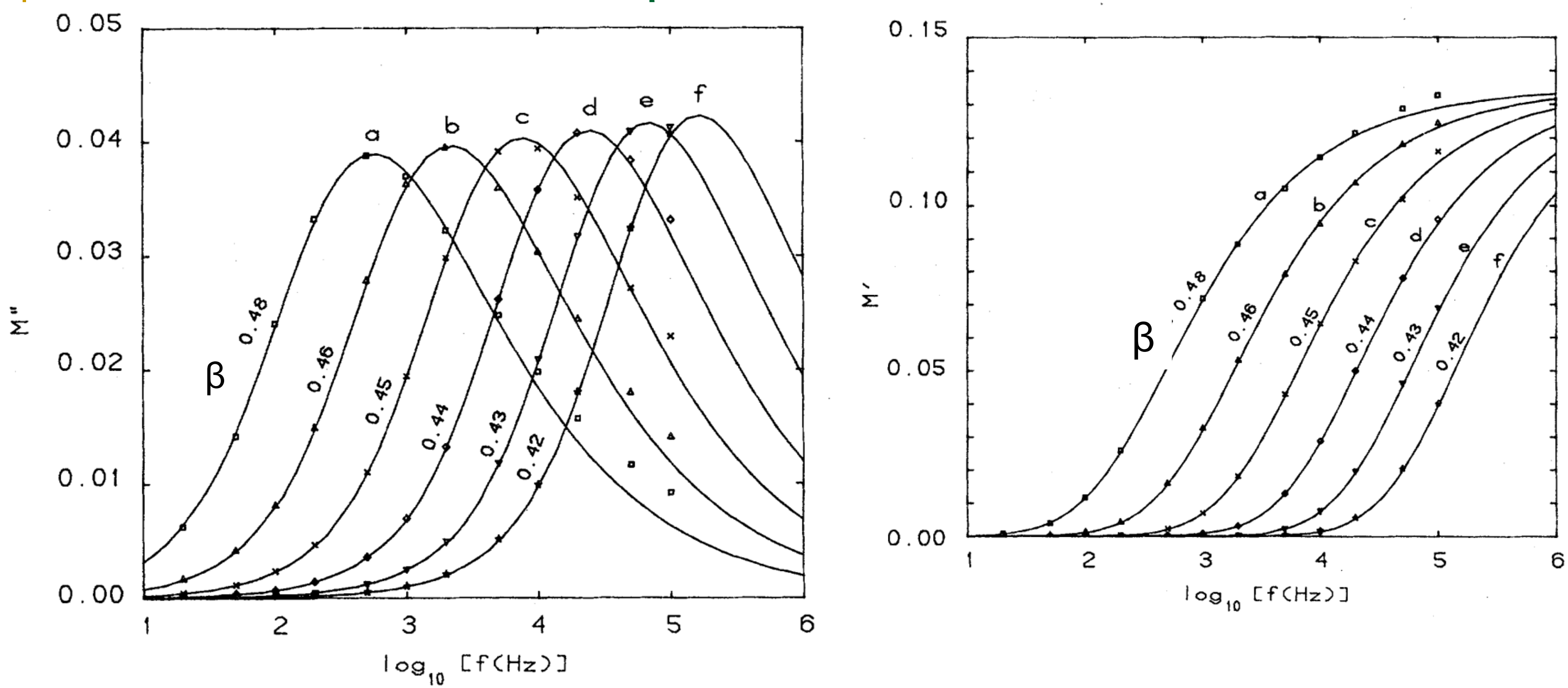
$$M^*(\omega)=M_\infty\left[1-\int_0^\infty dt\exp(-i\omega t)(-d\phi/dt)\right]$$

where M_∞ is the high frequency limit of M*.

In terms of ac conductivity:

$$\sigma(\omega)=\omega\epsilon_0\epsilon''(\omega)=\omega\epsilon_0[M''/(M'^2+M''^2)]\ ,$$

Connection with experiments



•Modulus spectra for lithium borate glass at increasing T (a) to (f). Note that β decreases slightly with increasing T.

•M*, which focuses on relaxation in the vicinity of Maxwell electrical relaxation, agrees reasonably well with Ngai model, but deviations occur at higher frequencies.

Ngai, Rendell, Jain, PRB (1984)

M* also shows scaling to master plots

Howell et al. (1974)

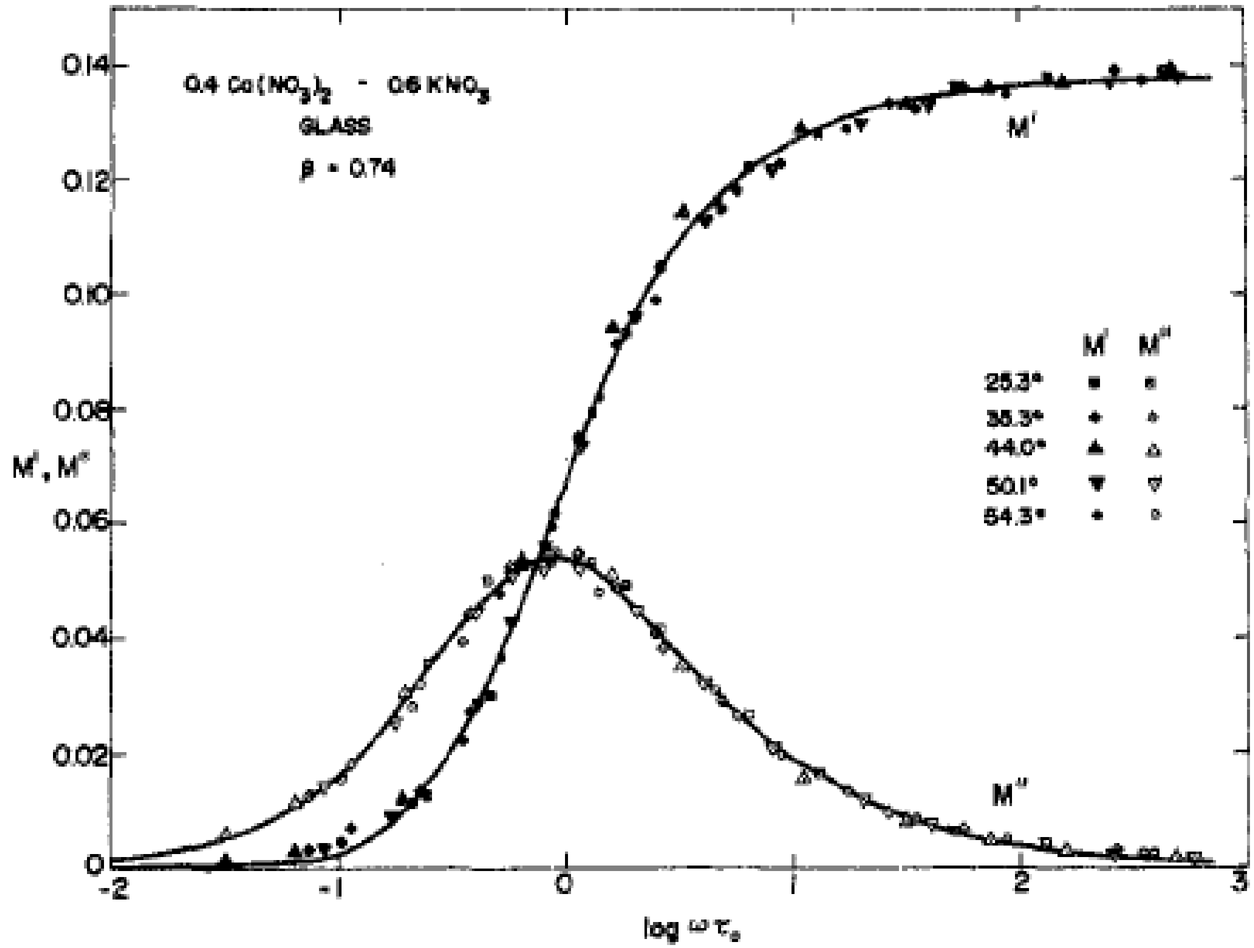
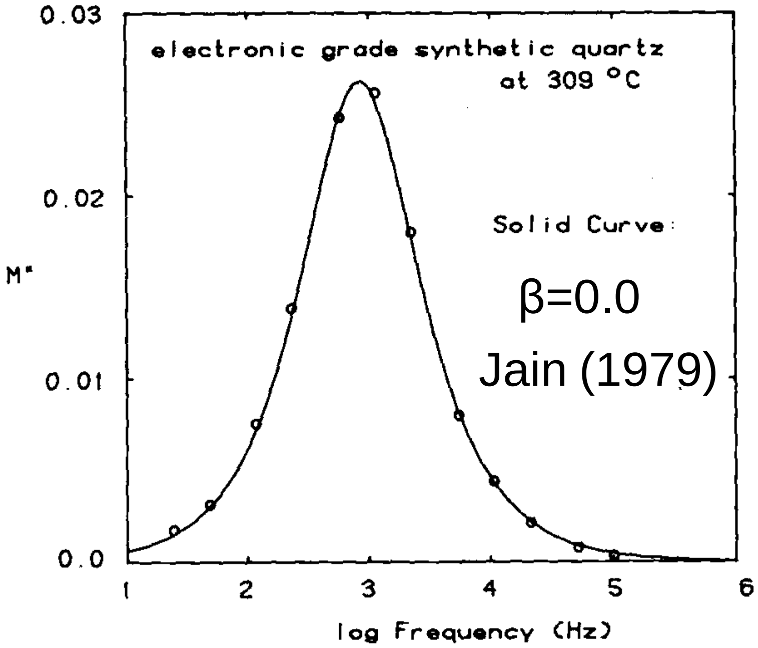
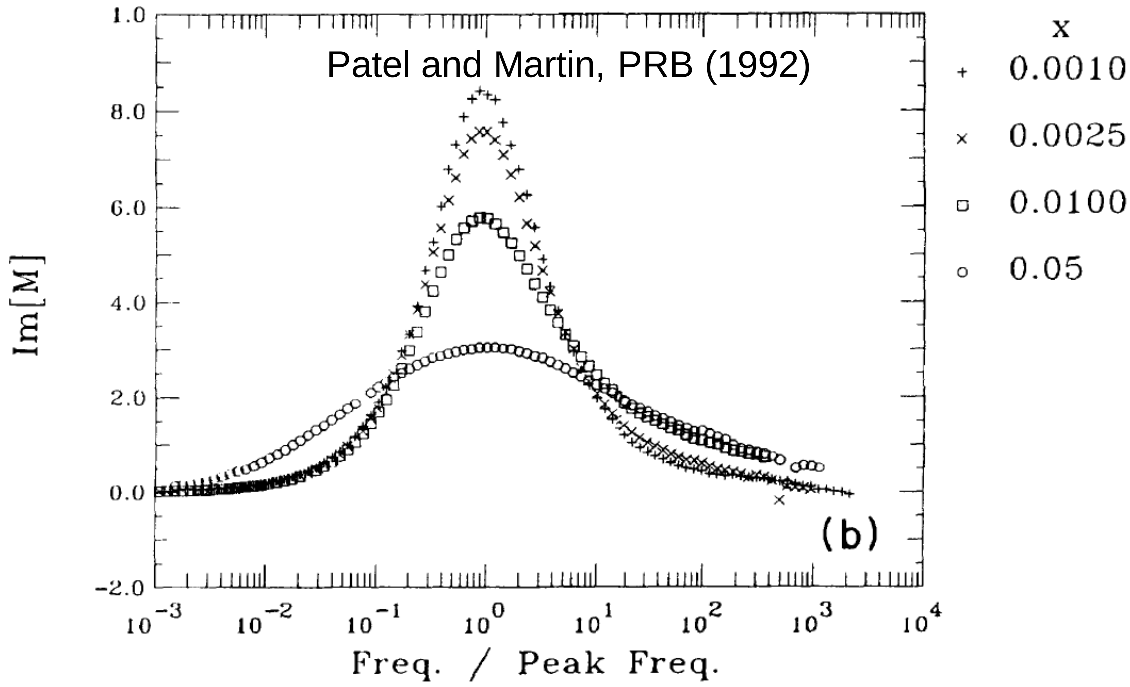


Figure 7. Real and imaginary parts of the electric modulus *vs.* reduced frequency $\omega\tau_0$ for $0.4Ca(NO_3)_2$–$0.6KNO_3$ glass.

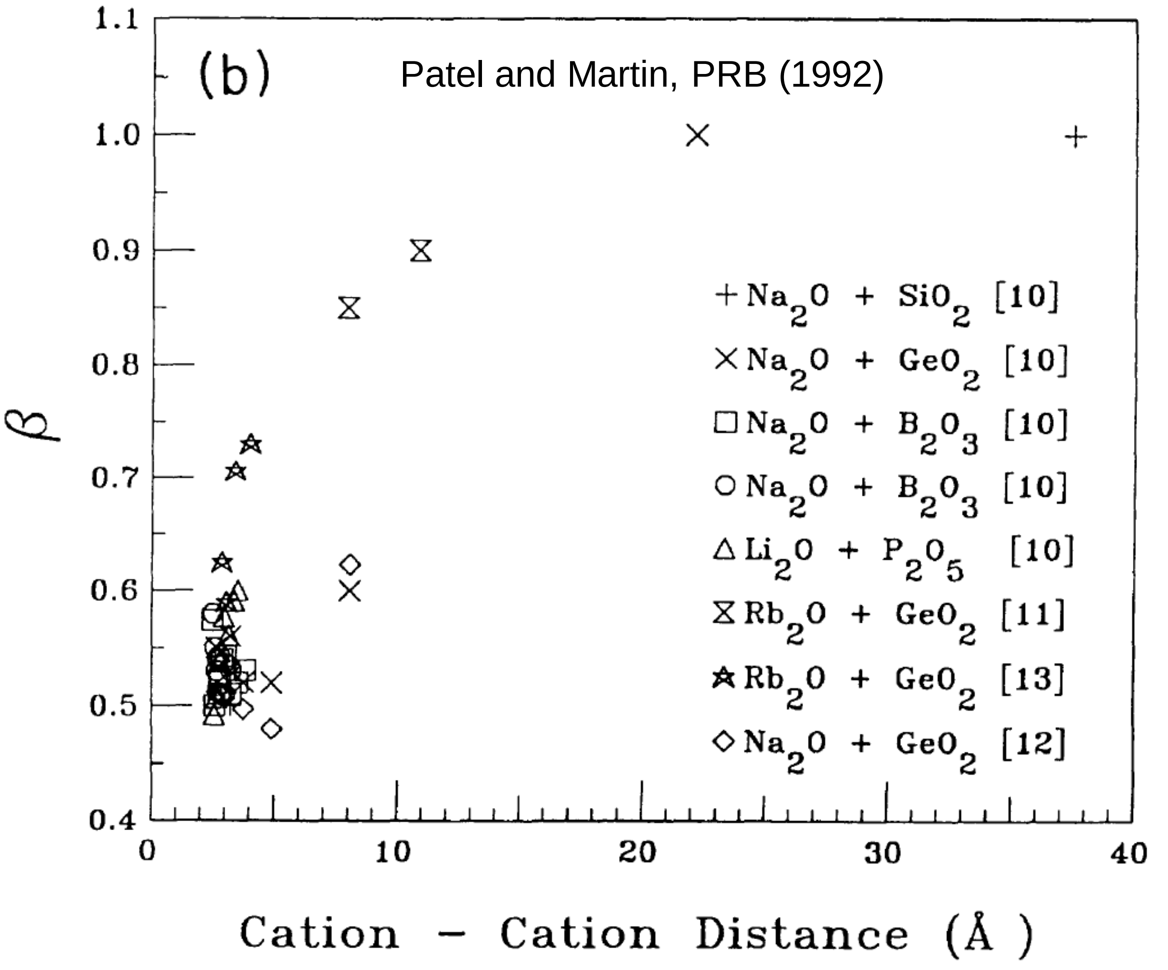
Composition dependence of M" peak

M" vs. normalized freq for $x(Na_2S)+(1-x)\ B_2S_3$ glass series



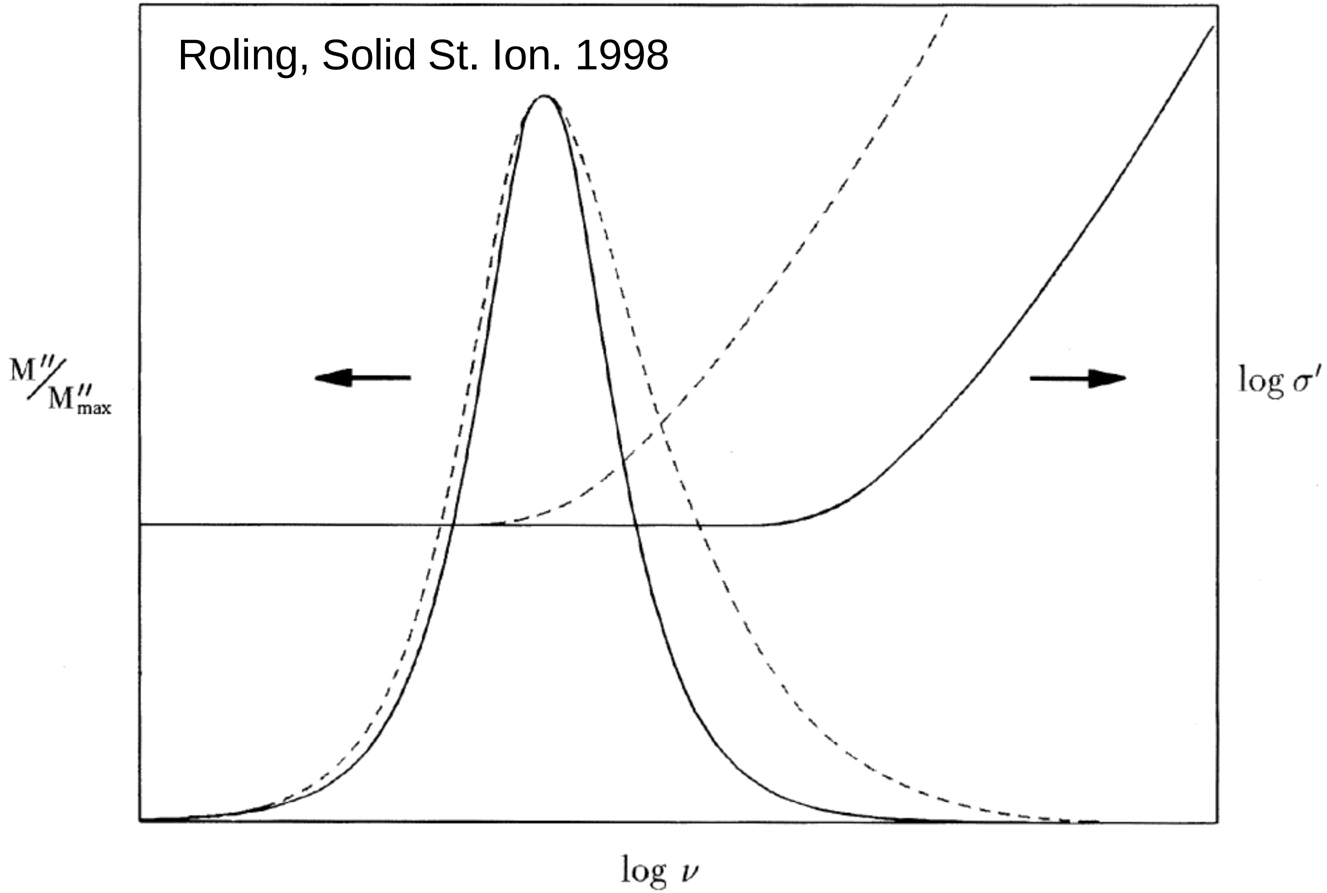


β represents strength of coupling among ions



Conductivity vs. M" spectra at low and high ion conc.

Dipolar dielectric loss peak, such as represented by BNN relation (Topic 1), and conductivity power law appear to be of different origin.



Schematic plot of the conductivity spectra and M" spectra of two glasses containing different number densities of mobile ions, *N* . *Solid lines: N is small, dashed lines: N is large.*

Summary at this point .

•Ion transport, responsible for electrical relaxation, in typical oxide glass is not just free hopping of ions.

•It is affected by structural heterogeneity as well as coulombic interactions with other species.

•The dispersion/relaxation in glass has universal features, which can be described often by master plots, especially when is concentration is not too low.

•Modulus formalism is convenient representation of relaxation in the vicinity of Maxwell relaxation time/frequency, but less useful at higher frequencies.