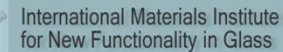# Advanced Vitreous State - Physical Properties of Glass

Lecture 27: Charge Conduction Properties of Glass:

Ionic Conduction in Glass - Part 3

*Intermediate Range Order Models
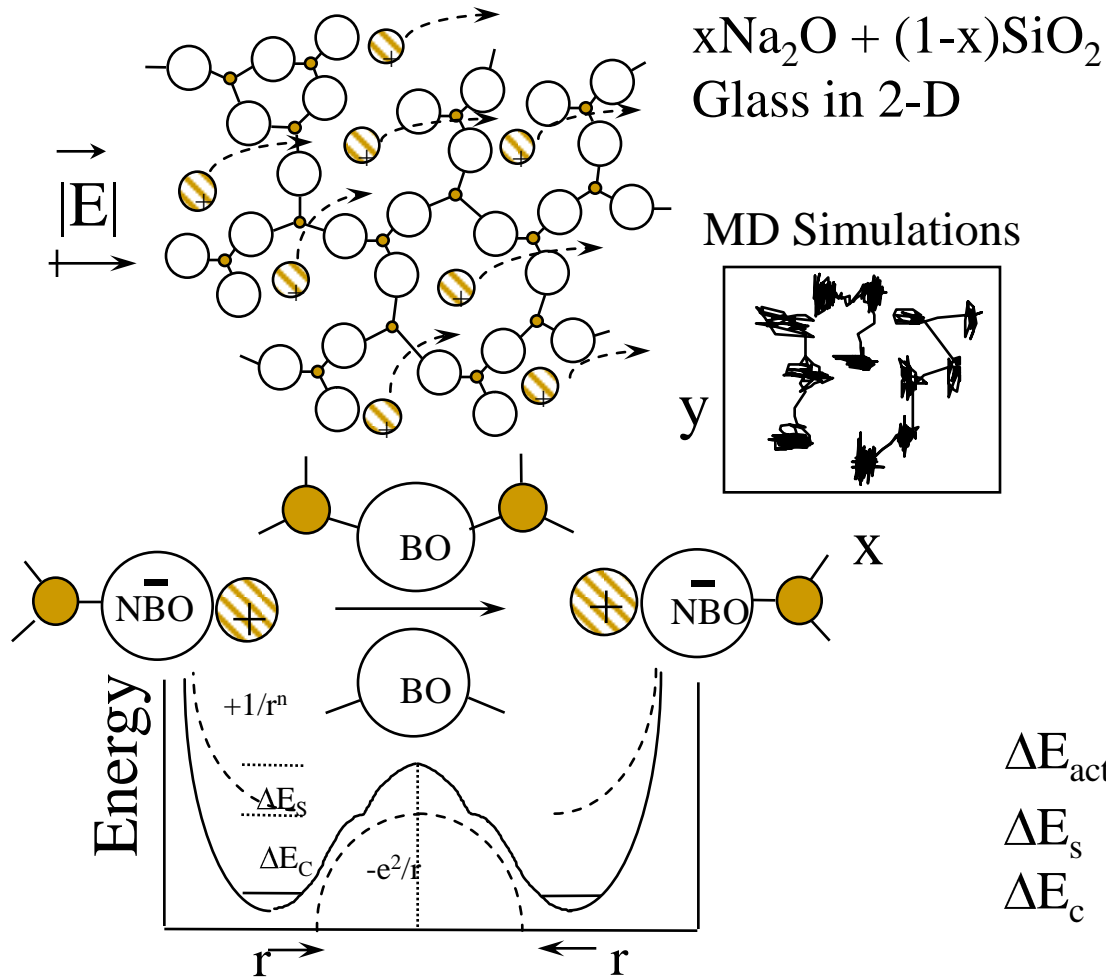and Effects of Frequency*

Steve W. Martin

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*swmartin@iastate.edu*
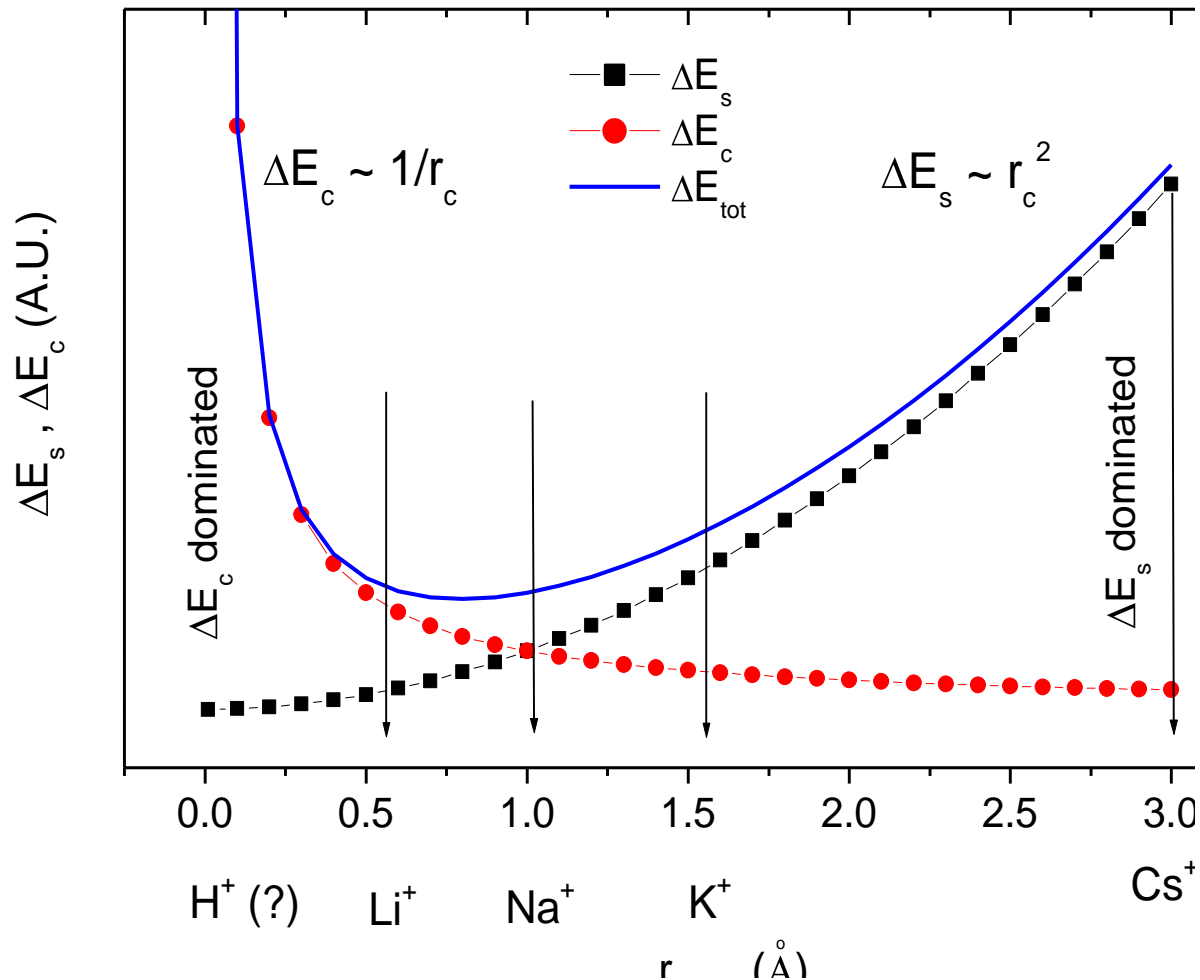
# Activation Energies of Ionic motion in glassy electrolytes

$xNa_2O + (1-x)SiO_2$
Glass in 2-D

MD Simulations

$\Delta E_{act} = \Delta E_s + \Delta E_c$

$\Delta E_s$ = Strain Energy

$\Delta E_c$ = Coulomb Energy

S.W. Martin, C.A. Angell, JNCS, 1983

# Cation Radius Dependence of $\Delta E_c$ and $\Delta E_m$

# "Rational" Models of the Activation Energy

- Both activation energies are non-zero and contribute to the total activation energy
- Anderson-Stuart[1] model calculation

$$\Delta E_C = \frac{\beta_{struct.} Z_c Z_a e^2}{\varepsilon_\infty} \left[ \frac{1}{(r_c + r_a)} - \frac{2}{\lambda} \right] \qquad \Delta E_s = \Delta E_m = 4\pi r_d G (r_c - r_d)^2$$

| x Na$_2$O + (1-x)SiO$_2$ | $\Delta E_s$ (calc) | $\Delta E_c$ (calc) | $\Delta E_{act}$(calc) | $\Delta E_{act}$[2] |
|---|---|---|---|---|
| 11.8 | 11.7 | 66.9 | 78.6 | 68.1 |
| 19.2 | 10.9 | 62.3 | 73.2 | 63.7 |
| 29.7 | 10.0 | 56.1 | 66.1 | 59.7 |

- Calculation shows that the $\Delta E_c$ term is the larger of the two energy barriers.
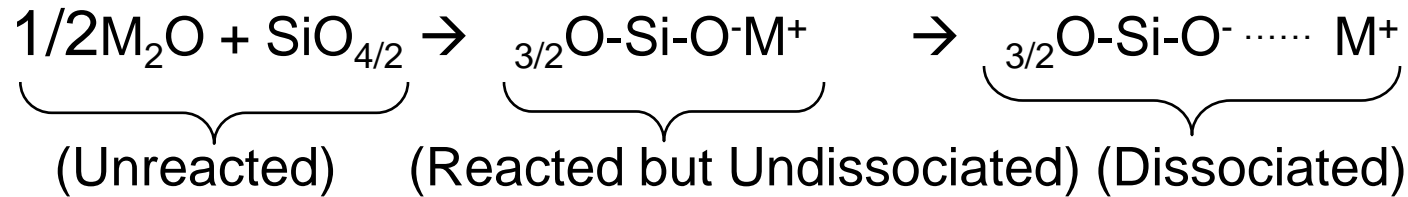- Weak-Electrolyte behavior?

[1] Anderson, Stuart, J. Amer. Cer. Soc., 1954
[2]  SciGlass 5.5, Average of many glasses

# Thermodynamic Models

- Glass is considered as a solvent into which salt is dissolved

- If dissolved salt dissociates strongly, then glass is considered a strong electrolyte

- If dissolved salt dissociate weakly, then glass is considered a weak electrolyte

- Coulomb energy term calculations suggest that the salts are only weakly dissociated, largest of the two energy terms

- Migration energy term is taken to be minor and weak function of composition

- Dissociation constant then determines the number of mobile cations available for conduction, dissociation limited conduction

# Weak Electrolyte model, *Ravaine & Souquet '80*

$$\frac{1}{2}M_2O + SiO_{4/2} \rightarrow \ _{3/2}O\text{-}Si\text{-}O^-M^+ \quad \rightarrow \ _{3/2}O\text{-}Si\text{-}O^- \cdots\cdots M^+$$

(Unreacted)   (Reacted but Undissociated) (Dissociated)

$$K_{diss} = a_M{+} \, a_{OM}{-} \, / \, a_{M2O}$$

$$\sim \ [M^+][OM^-]/a_{M2O} = [M^+]^2/ \, a_{M2O}$$

$$[M^+] \quad \sim \ K_{diss}^{1/2} a_{M2O}^{1/2} \equiv n$$

$$\sigma \quad = ze\mu n = ze\mu K_{diss}^{1/2} a_{M2O}^{1/2} \sim C \, a_{M2O}^{1/2}$$

$$\log K_{diss} \sim \ -Ne^2RT/4\pi\varepsilon_o\varepsilon_\infty (r_+ + r_-)$$

As $r_+$, $r_-$ increase, $K_{diss}$ increases
As $\varepsilon_\infty$ increases, $K_{diss}$ increases

# Intermediate Range Order models

- Models recognize that ion conductivity requires ion motion over relatively long length scales

- Ions must be able to move from one side of the electrolyte to the other

- Long range connectivity of the SRO structures favorable to conduction must exist

- Deep "traps" along the way must be infrequent and not severe

- Rather, low energy conduction "pathways" are thought to exist which maximize connectivity and minimize energy barriers and traps

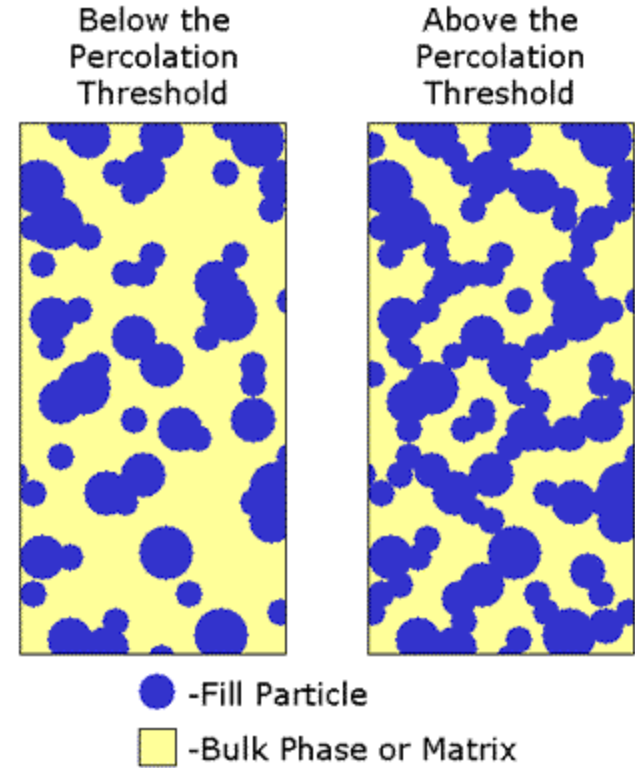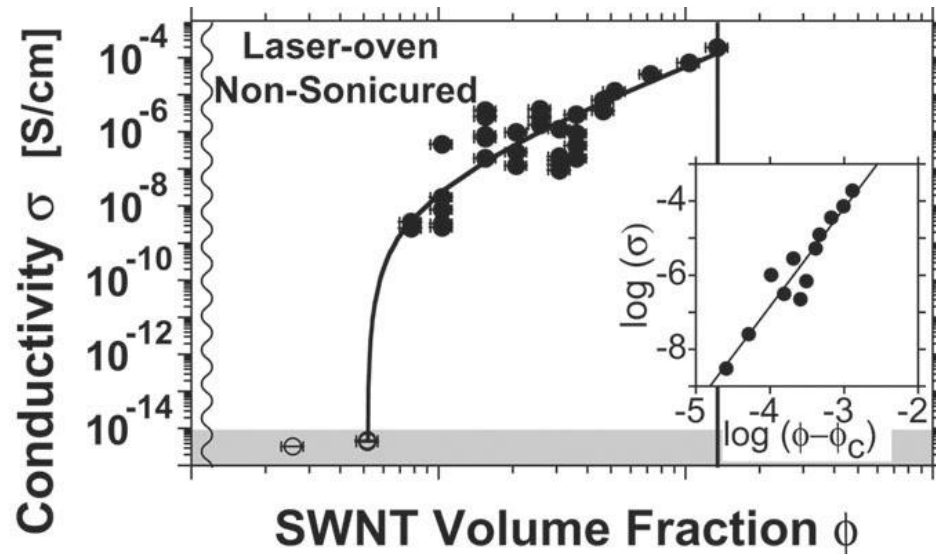- Cluster pathway model of Greeves '85, for example

# Intermediate Range Order models

- Cluster pathway model, *Greeves et al '85*

- Ionic structures in the glass group

- Covalent structures in the glass group

- This forms regions of high NBO concentration

- Causes conductivity to increase faster than simple uniform mixing would suggest
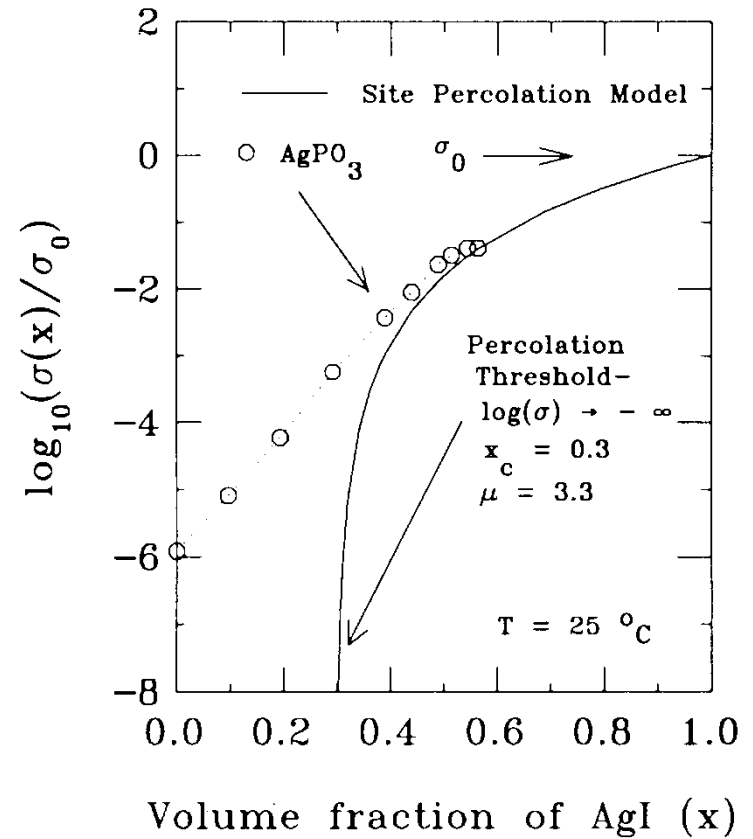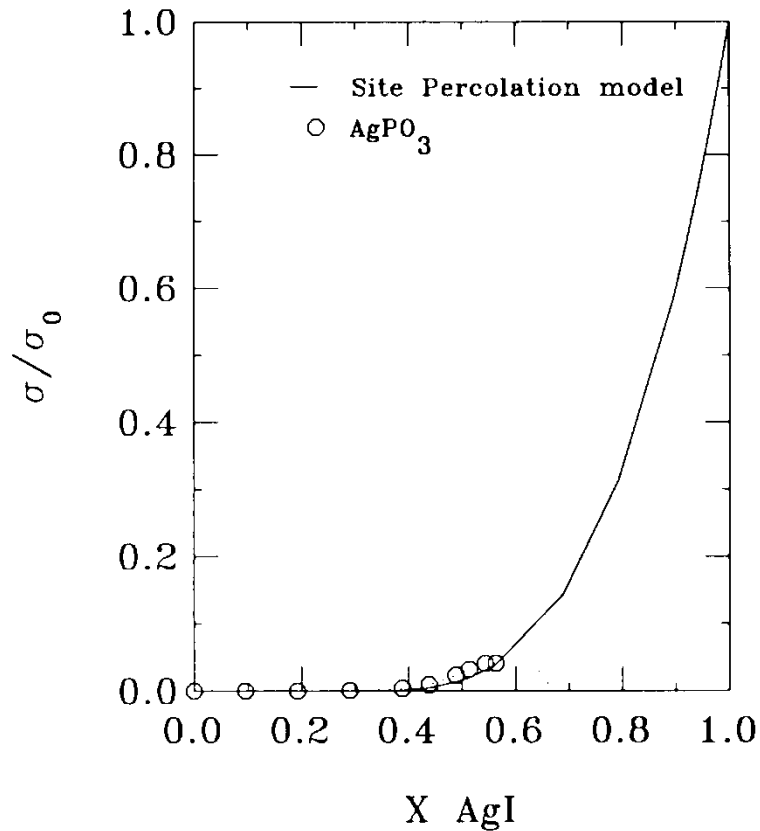
# Conductivity percolation



Below the Percolation Threshold

Above the Percolation Threshold
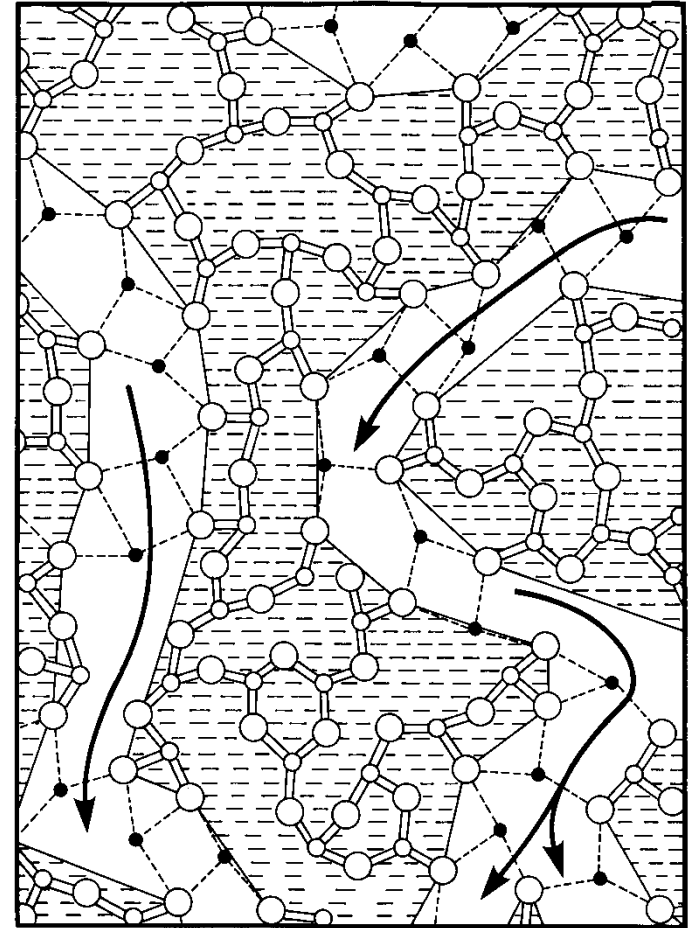
*http://www.tda.com/eMatls/images/Composites/percolation_scheme.gif*
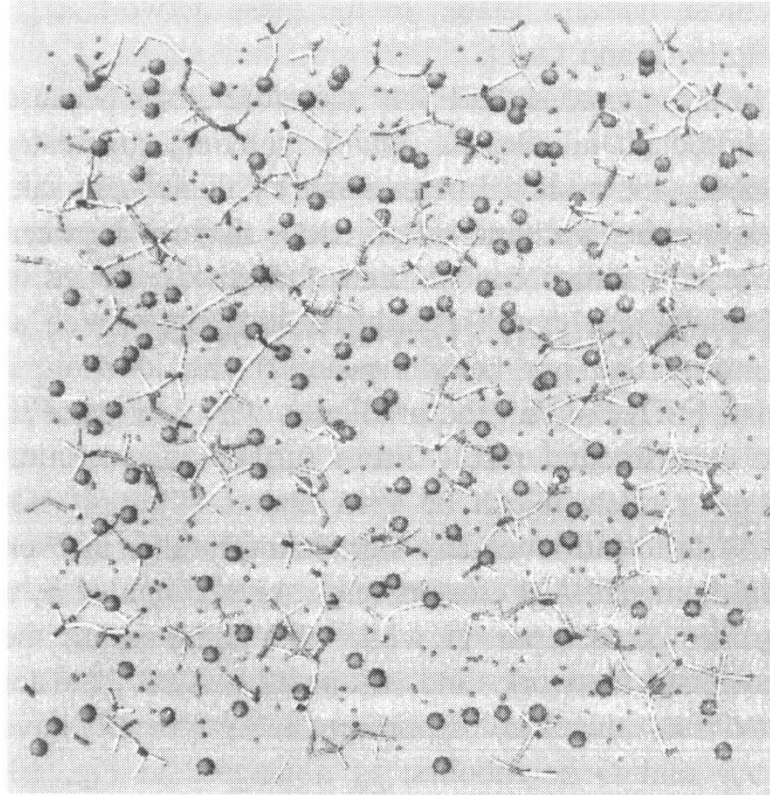
● -Fill Particle

▢ -Bulk Phase or Matrix

*http://www.physics.upenn.edu/yodhlab/images/research_CMP_percolation_plot.jpg*

# Conductivity percolation in AgI + AgPO$_3$

# RMC Modeling of AgI + AgPO$_3$, *Swenson et al. '98*



4.635 nm

# Intermediate Range Order models

- Microdomain models of conductivity

- Dopant salts such as AgI to oxide glasses, especially AgPO$_3$, are added to increase conductivity

- AgI is itself a FIC *crystal* above 150$^o$C

- Extrapolations of $\sigma$ to xAgI = 1 give ~ $\sigma_{AgI}$(298K)

- The question then is: Does the AgI create "microdomains" of $\alpha$-AgI giving rise to the high conductivity?

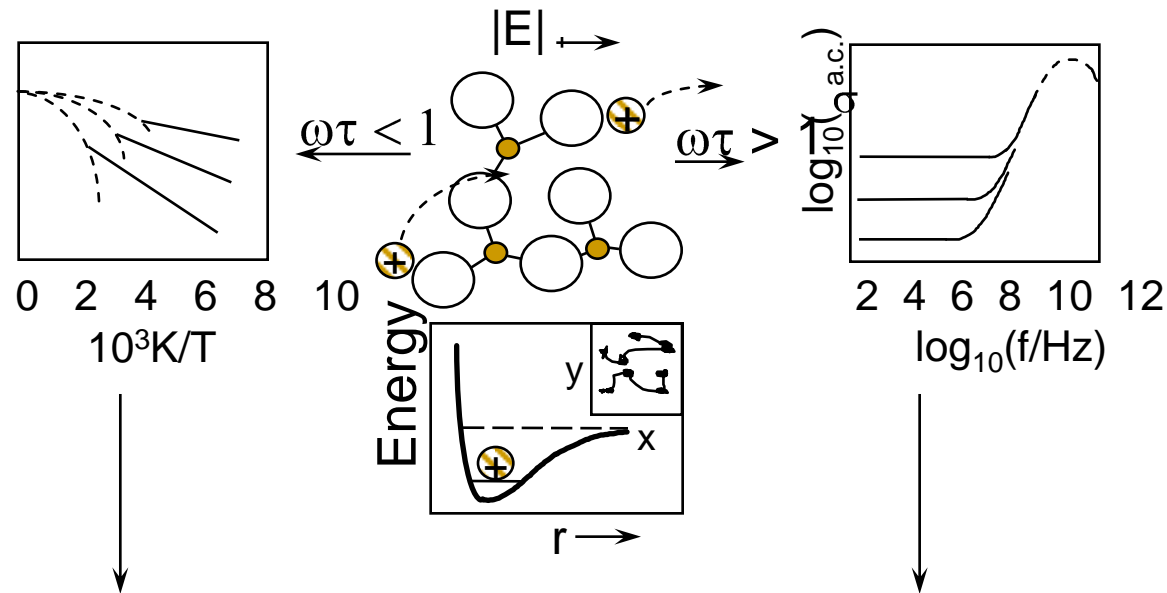# AgI Micro-domain model

- Most well known of all glasses is $xAgI + (1-x)AgPO_3$

- $AgPO_3$ is a long chain structure of -O-P(O)(OAg)-O repeat units

- Intermediate range structure is for these long chains to intertwine and as such frustrate crystallization

- Added AgI dissolves into this liquid without disrupting the structure of the phosphate chains

- Microdomain model then suggests that this dissolved AgI creates increasingly large clusters of $\alpha$-AgI between the phosphate chains

# AgI Micro-domain model
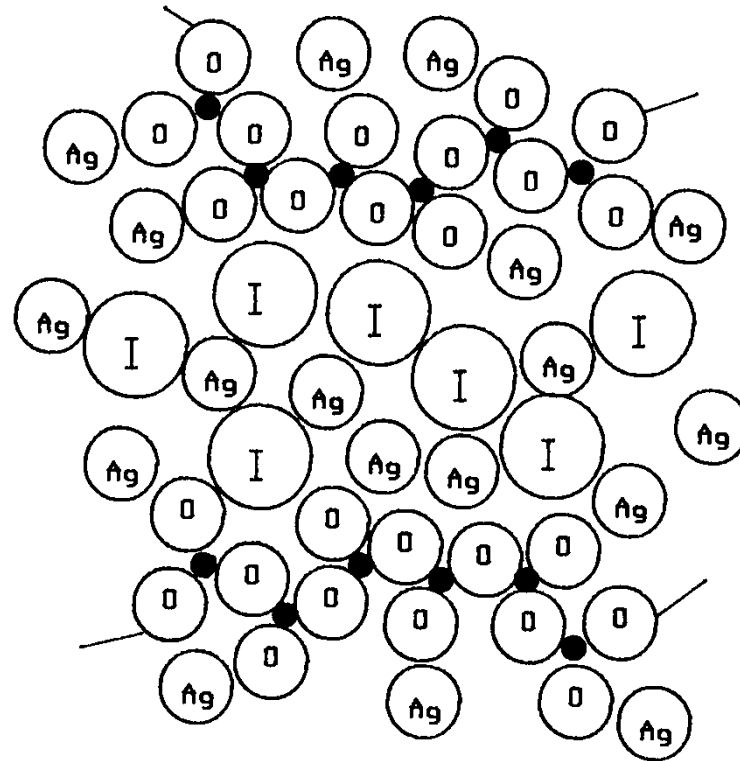
# AC versus DC ionic conductivity
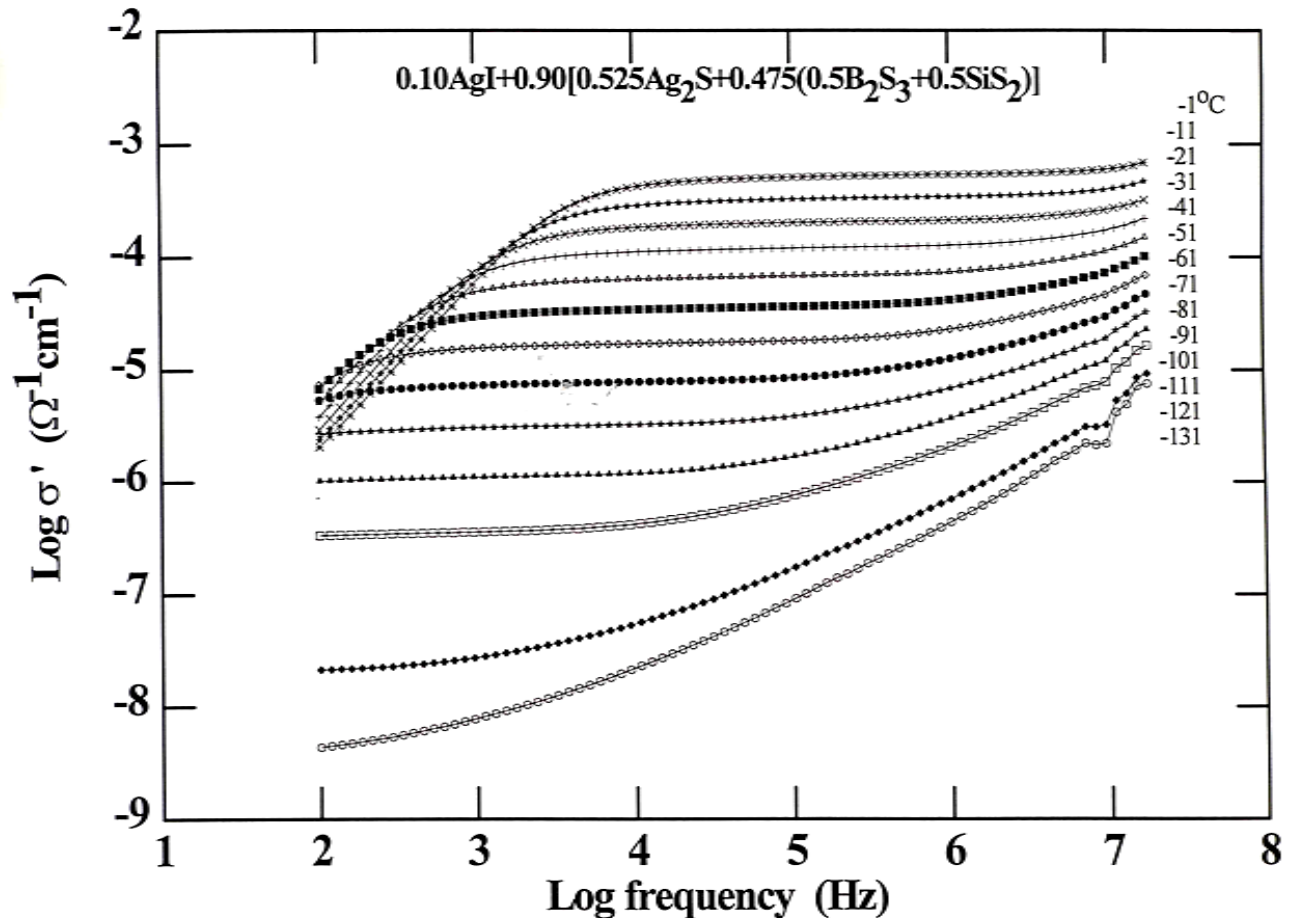


## D.C. Conductivity

*Anderson/Stuart - Coulomb & Strain Energies*

*Moynihan/Macedo - Debeye & Faulkenhagen Theory Modulus*

*Ravaine/Souquet - Weak Electrolyte*

*Malugani- AgI Micro domains*
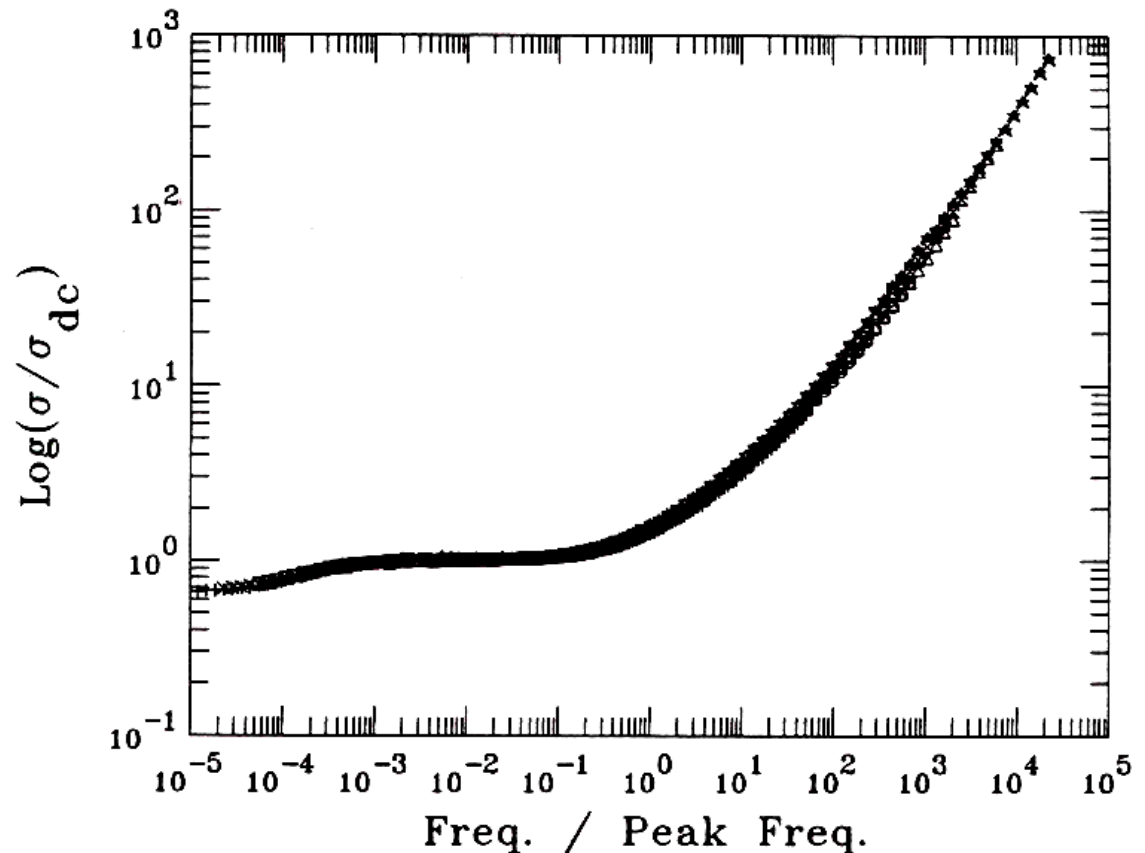
## A.C. Conductivity

*Ngai - Coupling Theory*

*Moynihan -*

*Dyre - Power Law*

*Funke - Jump Relaxation*

# AC ionic conductivity in glass
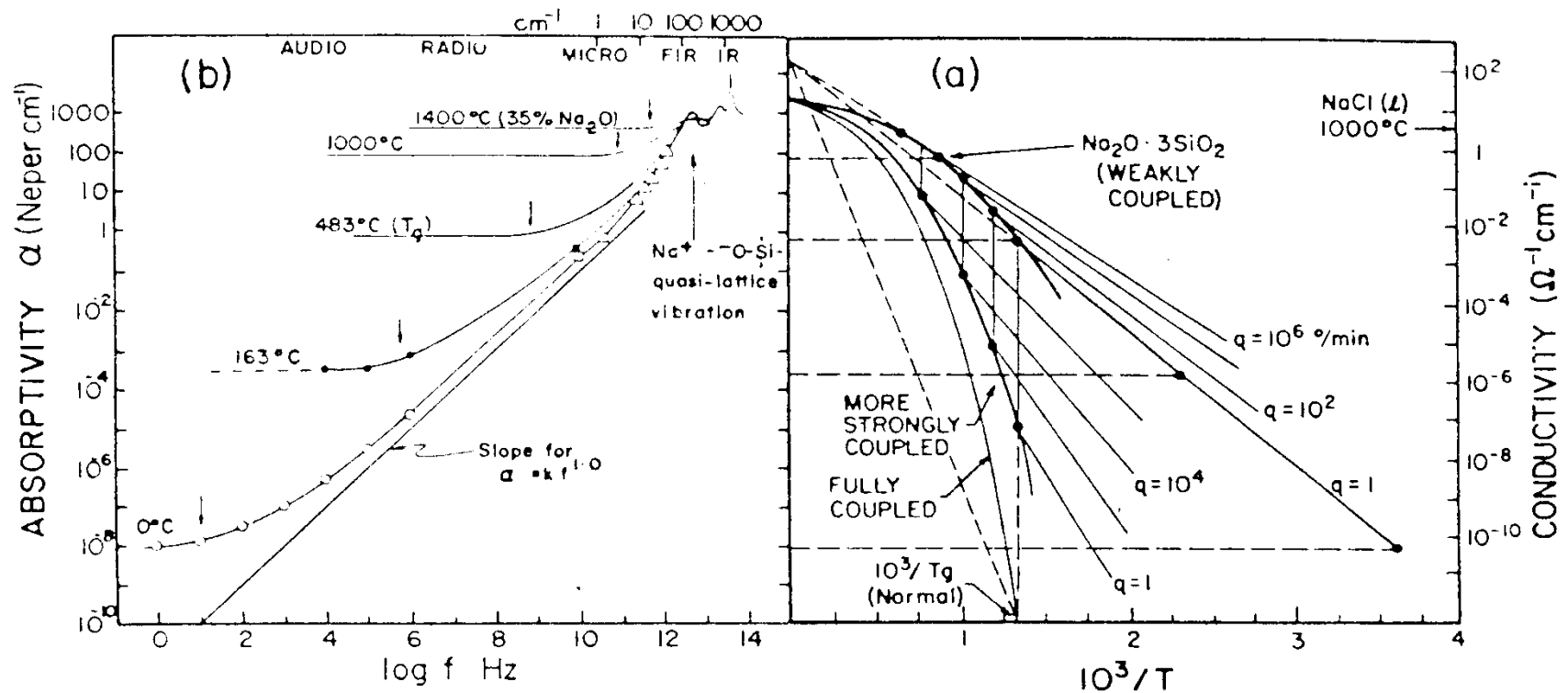


$0.10AgI + 0.90[0.525Ag_2S + 0.475(0.5B_2S_3 + 0.5SiS_2)]$

# AC ionic conductivity in glass

■ ## AC Conductivity in Glass

$$0.05K_2S + 0.95B_2S_3$$

# AC ionic conductivity in glass

■ **Connection to Far-IR vibrational modes,**

# AC ionic conductivity in glass

◆ Relationships between NMR and AC conductivity measurements

- 0.56Li$_2$S + 0.44SiS$_2$ FIC glass
- $\beta_{NMR}$ = 0.35  $\beta_\sigma$ = 0.48
- $\Delta E_{act}$ = 8.94 kcal/mol (7.95)
- $\tau_{0NMR}$ = 4.5 x 10$^{-14}$secs
- $\tau_{0\sigma}$ = 4 x 10$^{-15}$
- What is the origin of the difference in $\beta_{NMR}$ and $\beta_\sigma$ ?
- Why are the activation energies also different?
- Why are the pre-exponential factors different by a factor of 10?



0.56Li$_2$S + 0.44SiS$_2$

◇ 40 MHz
□ 12.2
○ 7
△ 4

(a)

$\ln[R_1(s^{-1})]$

$10^3/T$ (K$^{-1}$)
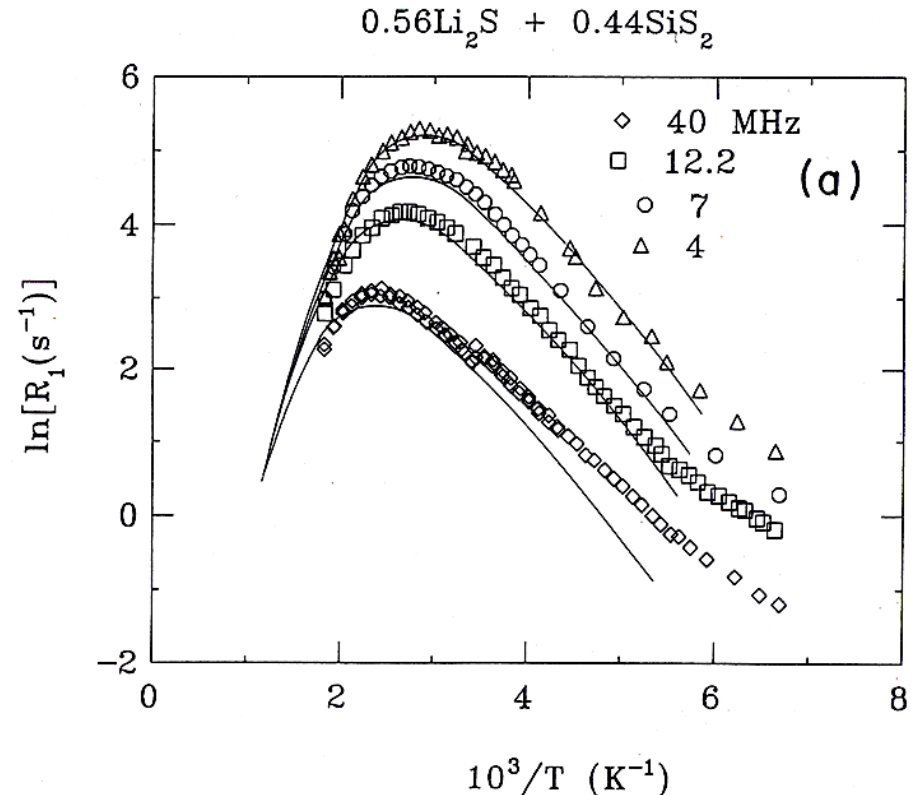
# AC ionic conductivity in glass

- **Average relaxation times**
  - For Conductivity and NSLR are:
  - Different in magnitude
  - Different in temperature dependence
- **What is the origin of the differences?**
- **Sigma and NSLR completely different processes?**
- **Is there a consistent formalism to treat both sets of data?**



$\tau(T)$ (s)

$xLi_2S + (1 - x)GeS_2$

$x = 0.35$

$x = 0.45$

Conductivity

NMR

$1000/T$ (1/K)
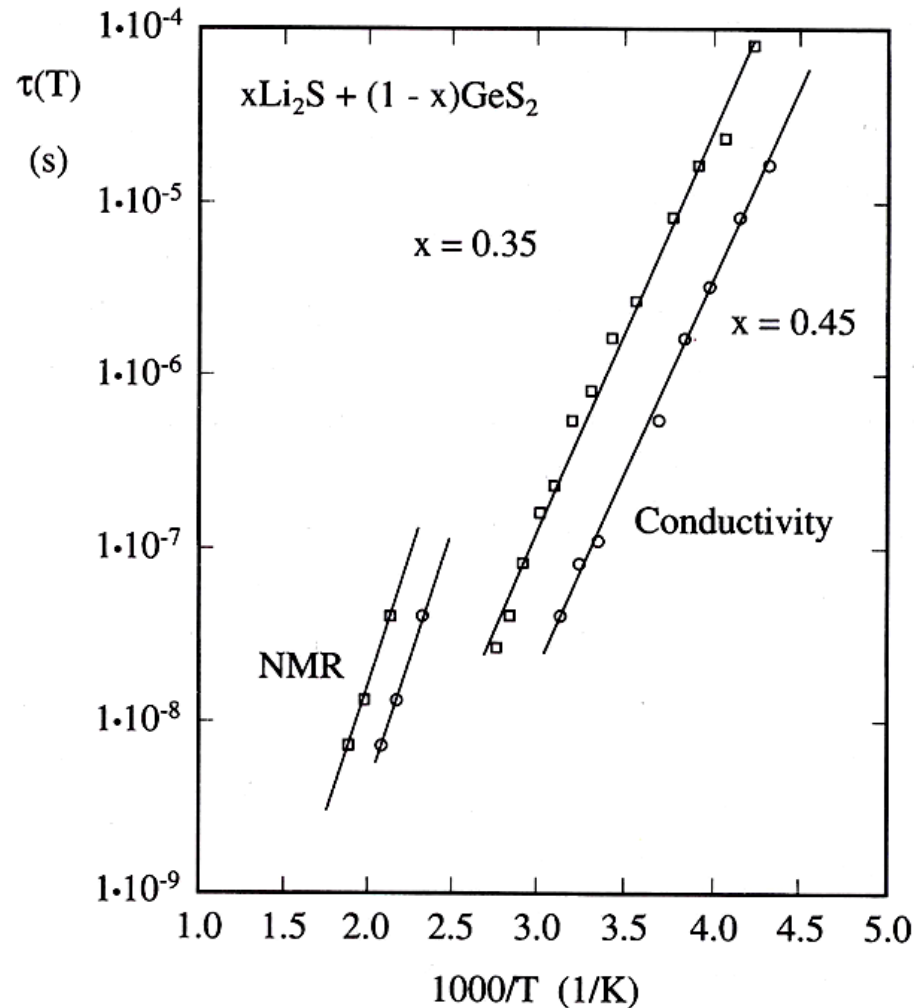
# AC ionic conductivity in glass - DAEs Treatment

- **Our fundamental hypotheses are that:**
  - Mobile ions reside in a disordered structure which create:
  - Variations in coordination number
  - Variations in bond lengths
  - Variations in bond strengths
  - Variations in jump distances to next cation site, which therefore
  - Create variations in activation energies from cation to cation in the glass
  - The distribution is hypothesized to be:
    - Continuous
    - Discrete
    - Centered about a mean
    - Symmetric to low and high energy values

# AC ionic conductivity in glass - DAEs Treatment

- Using a DAEs to treat ion conduction in glass is not new
- Von Schweidler used a DRTs as early as 1907
  - *Ann. Physik. **24**(1907)711.*
- Cole and Cole, Cole and Davidson reported log Guassian DAEs
  - *J. Chem. Phys. **9**(1941) 341*
- H. E. Taylor used a DAEs to describe the dielectric relaxation
  - Modeling $\varepsilon'$ and $\varepsilon''$ in soda-lime-silicate glass in 1955
  - *Trans. Fara. Soc. **51**(1955)873.*
- C. T. Moynihan used a log Guassian treatment
  - Modeling conductivity relaxation in CKN melts and glasses in 1972
  - *Phys. Chem. Glasses **13**(1972)171*

# Determination of the DAEs in Glass

- **Direct measurement through NMR NSLR data**

- **Conduction process is by the percolation through low barrier sites**

- **Conductivity will only measure the low energy barriers**

- **NSLR measures all cations, both contribute to NSLR $T_1$**
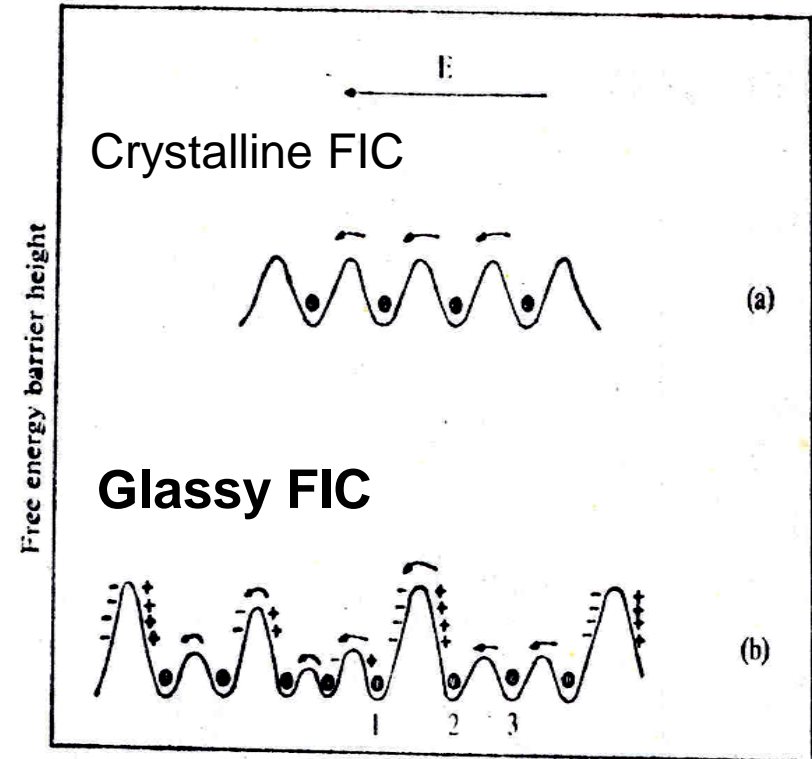


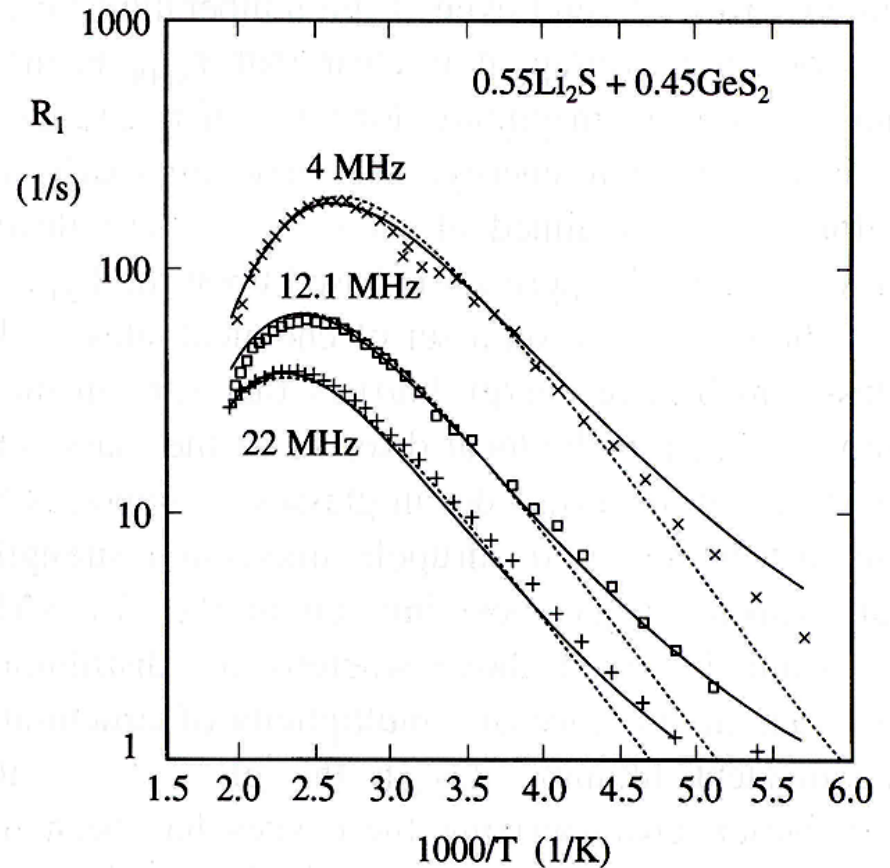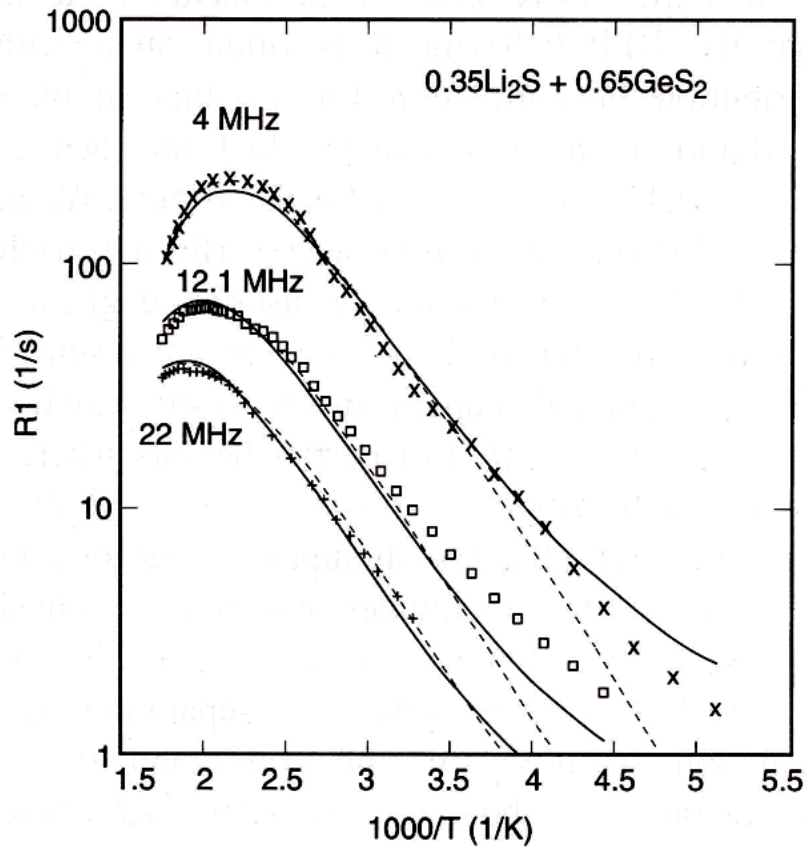*Stevels & Taylor DAEs model,*

# NMR NSLR Data

- Determination of the DAEs from NSLR $T_1$ measurements

$$1/T_1(\omega_L, T) \equiv R_1(\omega_L, T) = C \int_0^\infty \frac{\tau_a}{1 + \omega_L^2 \tau_a^2} + 4 \frac{\tau_a}{1 + 4\omega_L^2 \tau_a^2} Z_{NMR} dE_{NMR}$$

$$Z_{NMR}(E_a) = (1-y)\frac{1}{\sqrt{2\pi}E_b^2} \exp\left[-\frac{(E_m - E_a)^2}{2E_b^2}\right] + y\frac{1}{\pi}\left[\frac{E_1}{E_1^2 + (E_m - E_a)^2}\right]$$

- Gaussian DAEs with Lorentzian "tail", y ~ 0.2, to account for low temperature, high frequency "extra" relaxation

# DAEs from FIC $Li_2S$ + $GeS_2$ Glasses



0.35Li$_2$S + 0.65GeS$_2$

4 MHz

12.1 MHz

22 MHz

R1 (1/s)

1000/T (1/K)

0.55Li$_2$S + 0.45GeS$_2$

R$_1$

(1/s)

4 MHz

12.1 MHz

22 MHz

1000/T (1/K)

# DAEs from FIC Li$_2$S + GeS$_2$ Glasses

- Average of distribution shifts to smaller activation energies with increasing Li$_2$S

- Distribution does not change shape significantly, all have ~ same FWHM
    - 0.55 Glass is slightly narrower
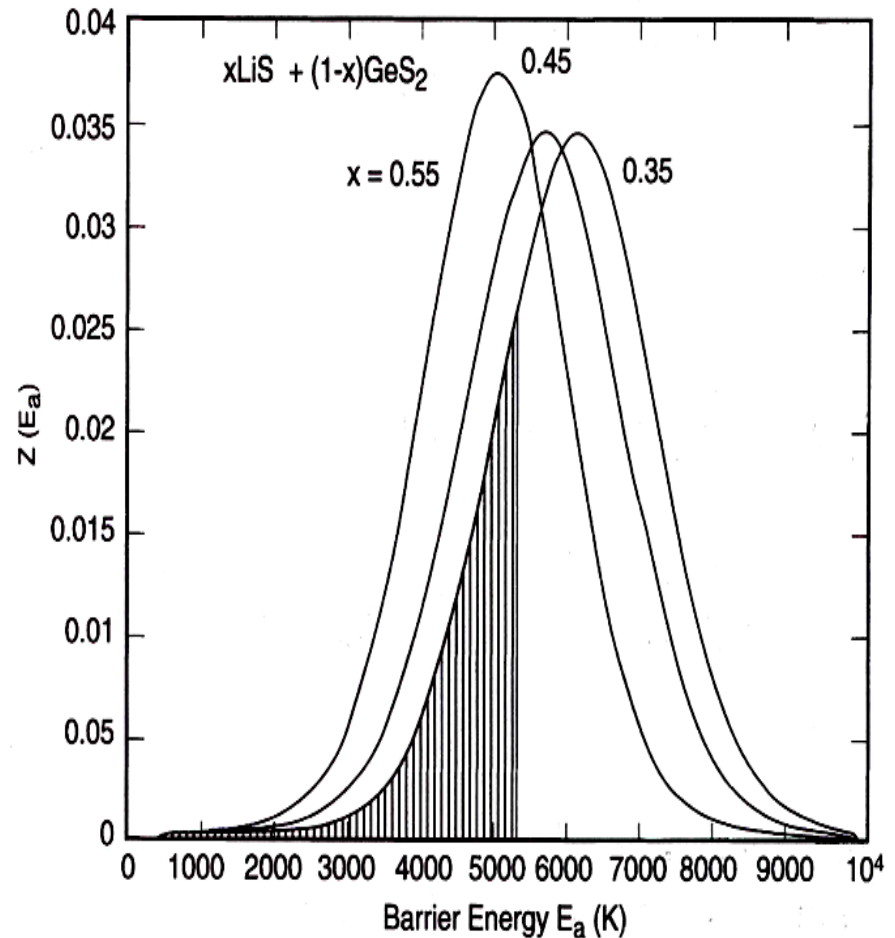
# Modeling of the DC conductivity from DAE (NSLR)

- $\sigma_{DC} = NPe^2d^2/6k_BT \; \tau_{av}$

- $r_a = r_{oa}\exp(-E_a/RT)$

- $r_{oa} = (E_m/2m)^{1/2}/d$

- $\tau_a = 1/6r_a$, assuming an octahedral site

- $\tau_{oa} = 2.7 \times 10^{-12}/(E_m/k_B)^{1/2}$

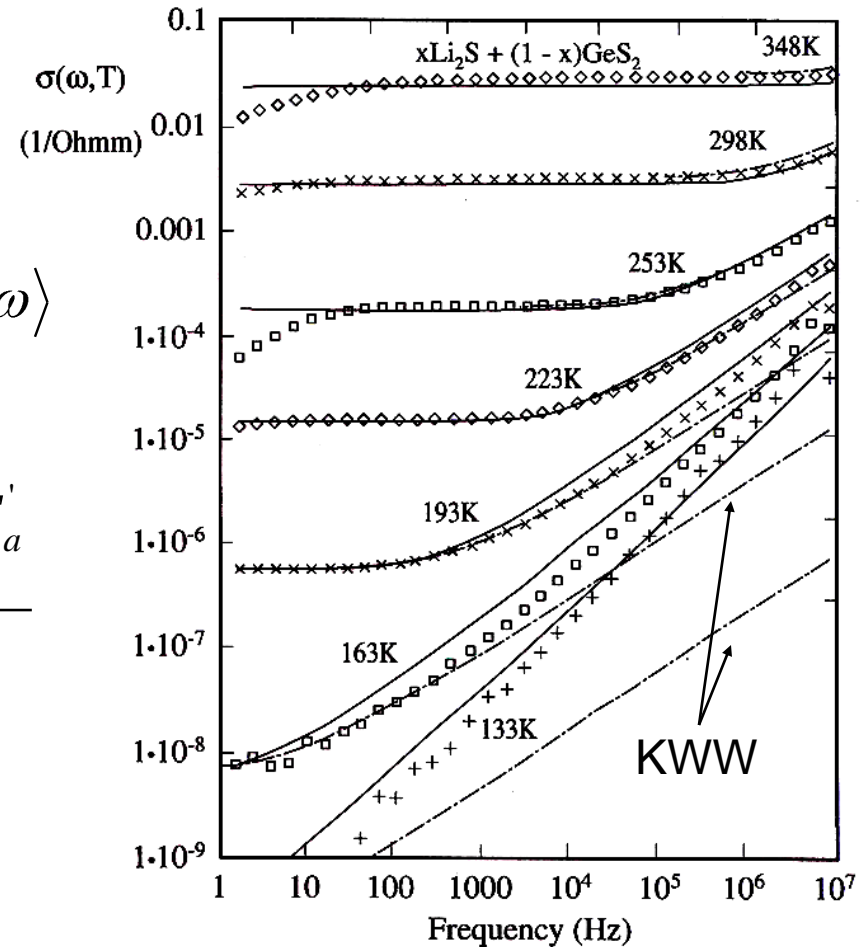$$\tau_{av} = (1/P)\int_{0}^{E_P}\tau_a(E_a/T)Z_{NMR}(E_a)dE_a$$
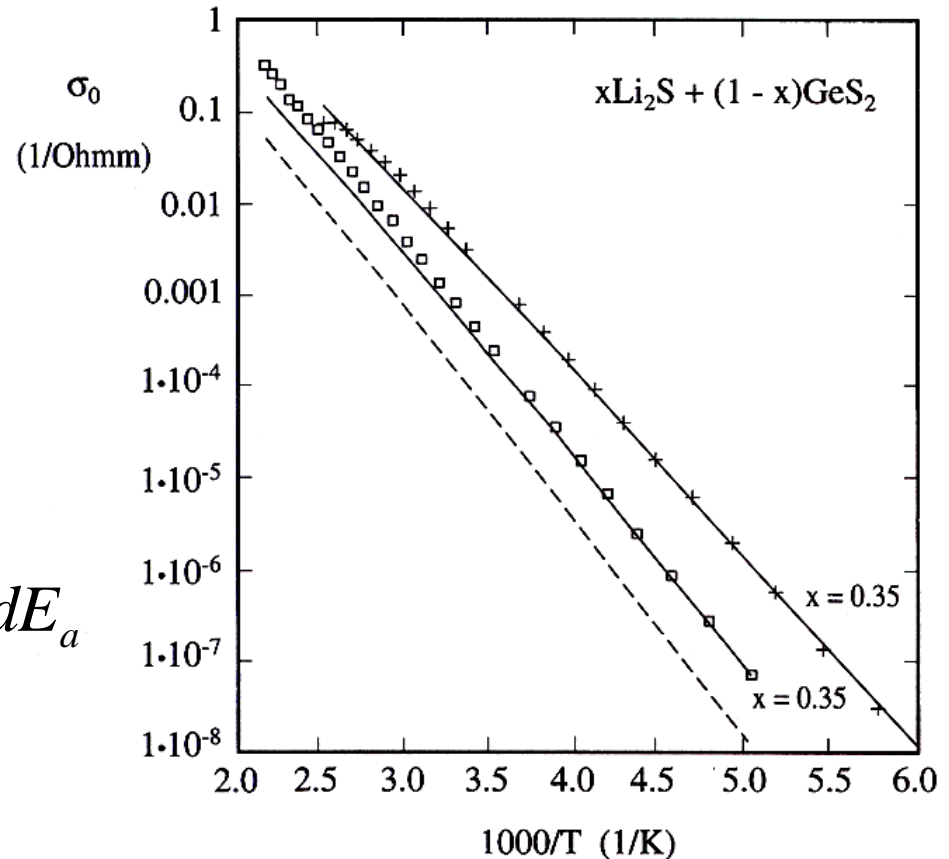
# Modeling of the AC Conductivity

- CTRW approximation of the AC conductivity
    - *Dyre et al*

$$\Big/ \sigma(\omega,T)/\sigma_{dc} + i\omega \stackrel{-}{=} \left\langle 1/\gamma_a(E_a,T) + i\omega \right\rangle$$

$$\frac{1}{\gamma_a(E_a,T)} = \frac{\displaystyle\int_0^{E_a} \tau_a(E_a',T) Z_{NMR}(E_a')dE_a'}{\displaystyle\int_0^{E_a} Z_{NMR}(E_a')dE_a'}$$

# Multiple FIC Dynamics in Glass

- "Multiple Channel" ion relaxation in FIC glasses

- $R_1$ data show evidence of multiple relaxation processes

- Fast process at low T, slower process at higher T

- Alkali thioborate glasses are speciated into tetrahedral borons and trigonal borons with NBS

- Are "slow" $Li^+$ ions associated with NBS?

- Are "faster" $Li^+$ ions associate with $BS_{4/2}^-$ groups?



0.7Li$_2$S + 0.3B$_2$S$_3$
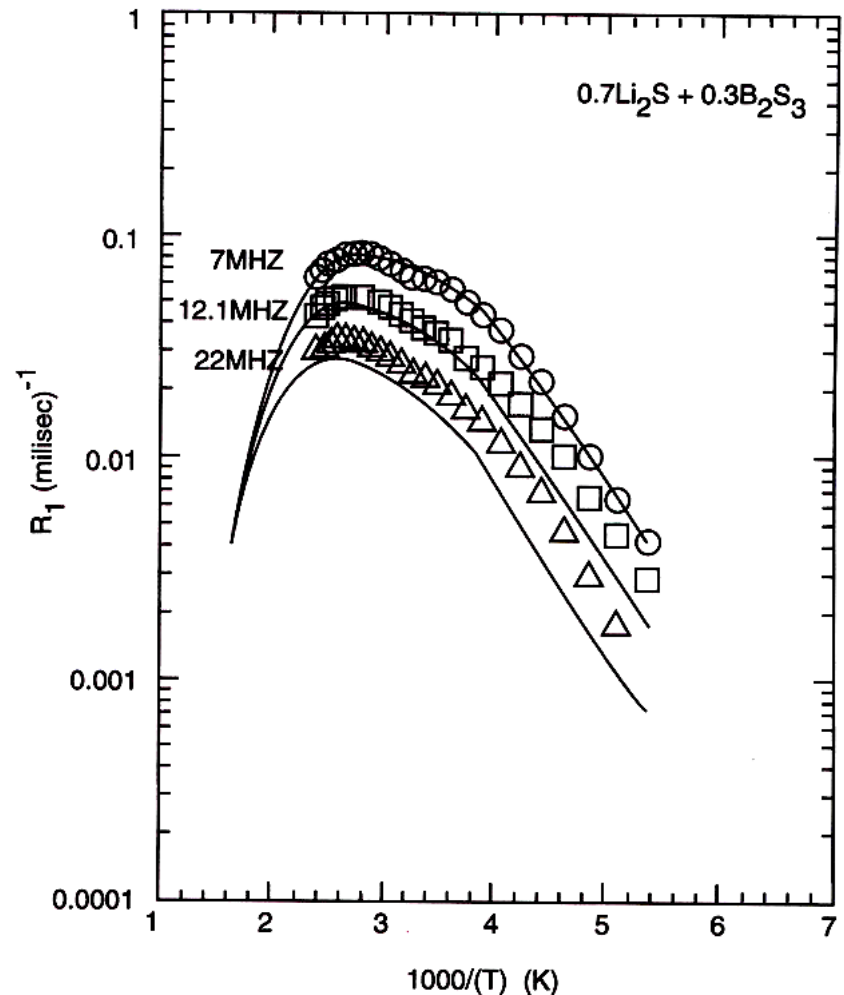
# Multiple FIC Dynamics in Glass

- Relaxation spectra of both mobile $Li^+$ ions and immobile frame work B ions were measured

- Multiple-channel relaxation was observed for $Li^+$ ions

- $BS_3$ and $BS_4$ units have different relaxation rates and hence difference DAEs to characterize their dynamics

- $N_4$ of $0.7Li_2S$ is 0.05

- Most $Li^+$ ions are associated with $BS_3^{3-}$ groups, as evidenced in the DAEs
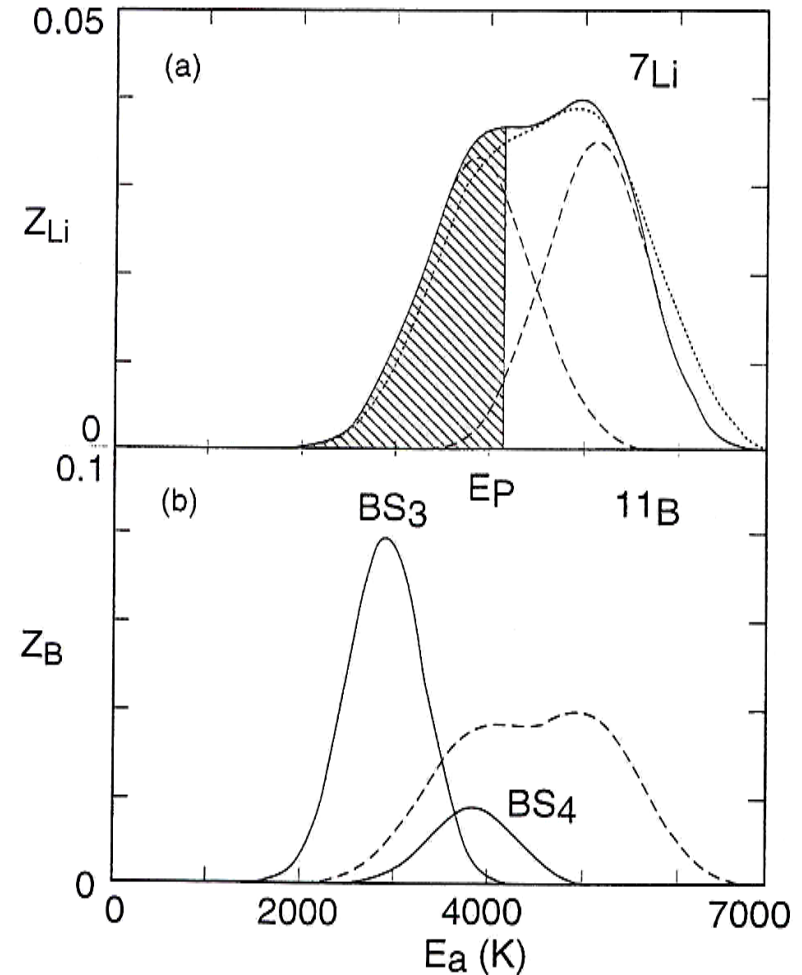
# Summary – Part 3

- The DAEs is an established formalism

- Reflects intrinsic disorder of glass

- In principle is a "calculable" property of glass once structure is known

- Accurately predicts (models) a variety of dynamic data, conductivity and NSLR

- "Naturally" treats multiple relaxation spectra

- Accurately models DC and AC conductivity data