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

Regimes of Ion Conduction in Common Glasses

Low-\( f \) Conductivity over a wide \( T \) range

\[ \sigma \sim \omega^s \]

\( s \sim 1 \Rightarrow \) nearly constant loss
Nowick: second universality

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)

$0.074\text{Li}_2\text{O}: 0.926\text{GeO}_2$

Lu and Jain (1994)
The clear delineation of the 3-D $\sigma$-f-T plots into two surfaces $\Rightarrow$ Two independent phenomena.
In most cases........

Empirically,

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

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

$\Rightarrow$

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

Extrapolation of 555.2 and 490 K data to 100 K
Small changes in composition affect the low-T and high-T $\sigma$ very differently. So the two $\sigma$'s should have different origins.

<table>
<thead>
<tr>
<th>Glass</th>
<th>ZrF4</th>
<th>HfF4</th>
<th>BaF4</th>
<th>LaF3</th>
<th>AlF3</th>
<th>LiF</th>
<th>NaF</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBLALi</td>
<td>48.22</td>
<td>---</td>
<td>22.41</td>
<td>4.64</td>
<td>3.54</td>
<td>21.19</td>
<td>---</td>
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<tr>
<td>ZBLAN(I)</td>
<td>54.82</td>
<td>---</td>
<td>25.00</td>
<td>4.04</td>
<td>3.16</td>
<td>---</td>
<td>13.52</td>
</tr>
<tr>
<td>ZBLAN(II)</td>
<td>27.40</td>
<td>27.40</td>
<td>19.76</td>
<td>3.06</td>
<td>3.19</td>
<td>---</td>
<td>19.19</td>
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<tr>
<td>ZBLA(I)</td>
<td>58.00</td>
<td>---</td>
<td>33.00</td>
<td>5.00</td>
<td>4.00</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>ZBLA(II)</td>
<td>59.45</td>
<td>---</td>
<td>30.87</td>
<td>5.69</td>
<td>3.99</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
Even for a binary glass system the composition dependence of the high-T and low-T $\sigma$ are very different. High-T $\sigma$ is much more sensitive to structure than low-T $\sigma$. 

$$x\text{Li}_2\text{O}:(1-x)\text{GeO}_2$$
High x glass at low T: Only NCL is observed

$24.7 \text{ mol } \% \text{ Li}_2\text{O} \text{ doped GeO}_2$

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 $\sigma(T)$ before the exponential increase cannot be understood by any high-$T$ ion hopping mechanism. NCL is superimposed with a discrete loss mechanism.

Comparison of NSR rate and $\sigma$ at low T

Heavy Metal Fluoride Glass

$\sigma$ detects only one kind of jellyfish, but NSR may find more than one. The pre-exponential factor is too low for single atom process $\Rightarrow$ 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 $\Delta$ due to structural disorder and ion-ion interactions.

$V$: Average potential energy barrier
$\Delta$: Asymmetry energy.
**ADWP relations**

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

\[
\phi(\Delta, V) = \frac{1}{\Delta_0 V_0} \cdot \text{sech}(V / V_0) \text{ and } \tau = \tau_0 \cdot \text{sech}(\Delta / 2KT) \cdot \exp(V / KT)
\]

**Approximations:** At low \( T \), (a) \( kT << V_m \) (b) \( V >> kT \) and (c) \( \Delta >> kT \).

\[
\sigma(\omega, T) \sim N T^\alpha \omega^\beta
\]

where \( \alpha \) is determined by the maximum asymmetry of ADWP, \( \Delta_{\text{max}} \).

\( \beta \sim 1 + (T / T_g) \)
Comparison of the ADWPC model with exptl. data

0.074 Li$_2$O : 0.926 GeO$_2$

0.0023 Li$_2$O : 0.9977 GeO$_2$

Typical fitting parameters:
- $R = 4\ \text{Å}$
- $N \approx 3 \times 10^{18}/\text{cm}^3$
- $V_m = 1000\ \text{K}$
- $\Delta_m = \Delta_0 + yT = 3K + 0.05T$
- $V_0 = 730\ \text{K} \tau_0 = 1 \times 10^{-6}\ \text{sec}$
Connection between $\sigma_{\text{low } T-\text{low } \omega}$ (IIIa) and $\sigma_{\text{RT-MW}}$ (IIIb)

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

\[ \text{Room Temp.} \]
\[ \sigma(\omega, T) = \omega^\alpha \exp \alpha'' T \]
\[ \alpha' \approx 1.1; \alpha'' \approx 4 \times 10^{-3}/K \]
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 $xY_2O_3 - (1-x)CeO_2$

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 $\omega = 10^{2.5}$ $\varepsilon''_{\text{max}} \uparrow$ for x: 0.05 < 0.1 < 0.2 < 0.5 ≈ 15 < 10 < 1 < 2 ≈ 5. $x_{\text{max}} = 2\approx5$ mol%.

Laughman & Jain, unpublished
Conclusions

1. There exist non-diffusive, non-vibrational, jellyfish fluctuations that determine $\sigma$ 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 IV: Very high f
- Vibrational loss region, with $s \approx 2$.

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

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

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

Regime I: High T - low f
- DC conductivity region, with $s = 0$.
Hope you had a chance to learn and feel relaxation!

Cheers!!