The Role of the Dispersion Parameter in Electrical Properties of Highly Disordered Insulating Materials

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The Role of the Dispersion Parameter in Electrical Properties of Highly Disordered Insulating Materials

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Outline

• Motivation
• Conduction in Crystalline Solids
• Localization
  • Defects
• Conduction in Disordered Solids
• Modeling of Charge Transport in Disordered Solids
  • Transients
  • Steady State
• The Dispersion Parameter
  • Equations and physical interpretation
  • Dispersive to normal transport transitions
• Conclusions
• Future work
Why?

• Connect microscopic processes to macroscopic behavior
• Explain anomalous/dispersive behavior
• Theory has applications from spacecraft charging to HVDC cable insulation
• Defines many different material properties and measurements characteristics

\[ \alpha(T) = \frac{kT}{E_c} = \frac{T}{T_c} \quad \alpha(E) = \frac{q\alpha E}{2kT_c} \]  

(Zallen, 1983)
Understanding Conduction - Crystalline

- Perfect periodic structure (long-range order)

Schrödinger’s Equation

\[ \frac{-\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r) = E\psi(r) \]

Bloch Functions

\[ \psi_k(r) = u_k(r)e^{i\mathbf{k}\cdot\mathbf{r}} \]
Understanding Conduction - Amorphous

Amorphous solids exhibit
- No long-range order
- Short-range order
- Atoms have equilibrium point

(Zallen, 1983)
Understanding Conduction - Localization

- Extended state wavefunction

\[ \psi_k(t) = u_k(r)e^{ik \cdot r} \]

- Localized wavefunction

\[ \psi \sim e^{-ar} \]

(Zallen, 1983)
Understanding Conduction - Localization

- Metal-insulator transitions with added:
  - Spatial separation (Mott transition)
  - Energetic disorder (Anderson Transition)
- Extended state to localized transition

<table>
<thead>
<tr>
<th>Transition</th>
<th>Metal side of Transition</th>
<th>Insulator side of Transition</th>
<th>Characteristic Energies</th>
<th>Change at the $M \rightarrow I$ Transition</th>
<th>Criterion for Localization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bloch</td>
<td>Extended</td>
<td>Extended</td>
<td>Bandwidth $B$</td>
<td>Partly filled bands $\rightarrow$ all bands filled or empty</td>
<td>—</td>
</tr>
<tr>
<td>Mott</td>
<td>Extended</td>
<td>Localized</td>
<td>Electron-electron ($\epsilon^{2}/r_{p}$) correlation energy $U$</td>
<td>Correlation-induced localization</td>
<td>$U &gt; B$</td>
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<tr>
<td>Anderson</td>
<td>Extended</td>
<td>Localized</td>
<td>Width $W$ of the distribution of random site energies</td>
<td>Disorder-induced localization</td>
<td>$W &gt; B$</td>
</tr>
</tbody>
</table>

(Zallen, 1983)
Defects

Types of Defects:
- Point
- Line (1D)
- Planar (2D)
- Volume (3D)

Doped Semi-conductors

Conduction

Valence

N-type

P-type

Vacancy

Substitutional (larger)

Frenkel Pair

Substitutional (smaller)

Interstitial
Understanding Conducting - Amorphous

Conduction mechanisms in amorphous insulators:

- Multiple Trapping and Thermally Assisted Hopping
- Variable Range Hopping and Radiation Induced Conductivity
- Percolation

(Zallen, 1983; Sim 2013)
Transient Anomalous Phenomena - Photoconductivity

- Random Walks
  - Spatially disordered lattice
  - Discrete hopping times
  - Requires ensemble averages of all possible spatial disorder

- Continuous Time Random Walks
  - Characterized by hopping-time distribution function
  - Walker moves on periodic ordered lattice but probability of hopping is given as a function of time
  - Disorder is contained in distribution function

(Gillespie, 2017; Zallen, 1983)
Transient Anomalous Phenomena - Photoconductivity

\[ I(t) \sim \begin{cases} \frac{1}{\Gamma(\alpha)t^{1-\alpha}} & t \ll t_{\text{transit}} \\ \frac{1}{-\Gamma(-\alpha)t^{1+\alpha}} & t \gg t_{\text{transit}} \end{cases} \]

Quick check: \(-(1 - \alpha) - (1 + \alpha) = -2\)

\[ \psi(t) \sim e^{-\tau} \]

\[ \psi(t) \sim t^{-(1+\alpha)} \]

(Zallen, 1983; Scher, 1975)
Transient Anomalous Phenomena – Permittivity and Conductivity

• Cole-Cole diagrams depict semi-circles or circular arcs
• Introduces the dispersion parameter through a geometrical argument
• Under DC conditions this gives a current of

\[
I(t) = \begin{cases} 
\frac{\varepsilon_0 - \varepsilon_{\infty}}{\tau_0} \frac{1}{\Gamma(\alpha)} \left( \frac{t}{\tau_0} \right)^{-(1-\alpha)} & t \ll t_{\text{transit}} \\
\frac{\varepsilon_0 - \varepsilon_{\infty}}{\tau_0} \frac{(-1)}{\Gamma(\alpha)} \left( \frac{t}{\tau_0} \right)^{-(1+\alpha)} & t \gg t_{\text{transit}}
\end{cases}
\]

\[
\varepsilon^* - \varepsilon_{\infty} = \frac{(\varepsilon_0 - \varepsilon_{\infty})}{(1 + i\omega\tau_0)}
\]

\[
\varepsilon^* - \varepsilon_{\infty} = \frac{(\varepsilon_0 - \varepsilon_{\infty})}{[1 + (i\omega\tau_0)^{\alpha}]}
\]

(Cole, 1941)
Transient Anomalous Phenomena – Permittivity and Conductivity

• Transient conductivity in constant voltage conductivity tests exhibit the same behavior as photoconductivity

\[ \sigma(t) = \sigma_P \frac{-t}{\tau_P} + \left\{ \sigma_{\text{disp}} t^{-(1-\alpha)} \theta(\tau_{\text{transit}} - t) + \sigma_{\text{trans}} t^{-(1+\alpha)} \theta(t - \tau_{\text{transit}}) \right\} + \sigma_{\text{DC}} \]  

(Wood, 2018)
Steady State Phenomena – DC Conductivity

Two regimes:

1. \( T \geq T_c \)
   - Multiple trapping dominates
   - \( \sigma \sim \exp(T^{-1}) \)

2. \( T < T_c \)
   - Variable range hopping dominates
   - \( \sigma \sim \exp(T^{-1/4}) \)

\[ \alpha(T) = \frac{T}{T_c} \]

(Dennison, 2008; Brunson, 2007)
Steady State Phenomena – Radiation Induced Conductivity

- Radiation induced conductivity is also defined by the dispersion parameter

\[ \sigma_{RIC} = k_{RIC}(T)D^\Delta \]

\[ \Delta = \frac{T_c}{T_c + T} = \frac{1}{1 + \frac{T}{T_c}} = \frac{1}{1 + \alpha} \]

(Gillespie, 2013; Tyutnev, 2006)
Anomalous Phenomena – Other

Experiments:
• Charge decay as modeled with a stretched exponential
  \[ I_{ph}(t) = I_{ph}(0)e^{-\left(\frac{t}{\tau}\right)^\beta} + \text{constant} \]
  - \( \beta = 1 - \alpha \)
• Surface voltage potential
• Luminescence
• Secondary electron yield

Modeling Approaches:
• Fractional dynamic equations
• Effective medium approach

Fractional Fokker-Planck Equation
\[ \frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left( -\frac{\partial}{\partial x} \frac{F(x)}{m\eta_x} + K_\alpha \frac{\partial^2}{\partial x^2} \right) P(x, t) \]

Fractional Derivative
\[ y = \frac{1}{2} \cdot x^2 \]

Fractional Diffusion Equation
\[ \frac{\partial}{\partial t} P(x, t) = D_t^{1-\alpha} \frac{\partial^2}{\partial x^2} P(x, t) \]

(Metzler 2004)
Physical Significance of $\alpha$

Word of warning:

• Difficult to extract due to multitude of underlying factors leading to the same experimental behavior
  • Charge transport depends on parameters that are statistically distributed, leading to broad distributions of event times
  • Small variations $\rightarrow$ broad distributions

“However complicated the form of the transition rates and the details of the molecular charge transfer, it is assumed that these rates depend sensitively on a number of parameters that are statistically distributed. Thus, even rather mild variations of some system parameters ‘map’ onto a broad distribution of transition rates. This mapping is not unique. A number of different parameter dispersions can produce very similar transition rate distributions.”
  (Pfister, 1978)

To obtain a broad dispersion of transit times (or featureless current trace) a carrier must be captured approximately once in a trap whose mean release time $\tau_{r,i}$ is approximately equal to the empirical transit time $\tau$. This is called the critical trap criterion (CTC).
  (Schmidlin 1977)
Density of States - Exponential

- Exponential energetic density of states in mobility gap
- Most commonly used in the literature
- Otherwise Gaussian is considered
  - Math considerably more complex (often numerical)

(Adhikari, 2018)
Physical Significance of $\alpha$

- **Hopping**
  - CTRW
  - Average site distances
  - Transition rates
- **Multiple trapping**
  - Transport equations
  - Capture and release rates
- **Percolation**
  - Transitions related to critical fractions
  - Monte-Carlo Simulations
- **Thermalization**
  - Physical interpretation of current traces

(Zallen, 1983; Sim, 2013)
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Figure 1 - Distribution of injected electrons in traps after one trapping time, plotted on a linear scale. The zero of energy isetime conduction band mobility edge.

Figure 2 - Distribution of electrons at time $t$, on a log scale, many trapping times after the injection pulse. In the text the peak in the density at $\epsilon(t) = kT \ln v t$ is treated as being sharp, although in practice it is always rounded.

(Sim, 2013; Tiedje, 1981)
Physical Significance of $\alpha$ - Thermalization

- Dispersive transport occurs during thermalization of charge
- Centroid of charge is located at the demarcation energy
- Demarcation energy equals the equilibrium Fermi level when equilibrium is reached
- If $DE > TE$ then downward hopping dominates
- If $DE < TE$ then VRH-like transport occurs (up hop)
Physical Significance of $\alpha$ – Dispersive to Normal Transport Transition

• Transition occurs at $\alpha = 1$
• Dispersive to normal transport transition occurs at when $T = T_c$
• $T_c$ is temperature at which states are "frozen in"

$$\alpha(T) = \frac{kT}{E_c} = \frac{T}{T_c} \Rightarrow \alpha = 1 \quad T_{\text{Transition}} = T_c$$

Temperature dependence of hole transport PVK and 3Br–PVK. Representative current traces are shown (after Pfister and Griffiths 1978). (Pfister, 1978)
Physical Significance of $\alpha$ – Dispersive to Normal Transport Transition

- Transition occurs at $\alpha = 1$
- Dispersive to normal transport transition occurs at when $E = E_{\text{Transition}}$
- $E_{\text{Transition}}$ denotes onset of electrostatic breakdown

$$\alpha(E) = \frac{qaE}{2kT_c}$$
$$\alpha = 1$$
$$E_{\text{Transition}} = \frac{2kT_c}{qa}$$

$$F_{\text{min}} = \frac{\Delta E}{qa}$$

(Andersen, 2017; Matsui, 2005)
LDPE as an example

- $T_c = 268$ K from $\sigma(T)$
- $\beta$-phase transition at $\sim T_c$
- ESD onset and dispersive to normal transport transition at $E \sim 100$ MV/m
- RIC measurements predict $T_c \sim 255$ K

$T_{\text{Transition}} = T_c$

$E_{\text{Transition}} = \frac{2kT_c}{qa}$

(Wood, 2018; Brunson, 2007; McCrum, 1967; Matsui, 2005; Andersen, 2017)
Conclusions

• Dispersion parameter describes many physical phenomena
  • AC and DC conductivity
  • Photoconductivity and radiation induced conductivity
  • Transitions associated with ESD onset, glassy transition temperature, normal
to dispersive transport

• Ratio of thermal or field energy to characteristic energy (width)

• The dispersion parameter is a wonderful tool to understand
  measurements (macroscopic effects)

• For deeper physical understanding (microscopic effects) a detailed
  knowledge of the material must be established first
Future Work

• Link measurements of LDPE in the literature through the dispersion parameter
  • Cole-Cole diagrams of permittivity
  • DC conductivity plots
  • ESD onset and association with dispersive/normal transport transition
  • Temperature dependent conductivity and transition

• Measurements of charge propagation via PEA

• Measurements of temperature dependent conductivity via CVC
Constant Voltage Conductivity Chamber

\[ V = I \left( \rho \frac{L}{A} \right) \]

Ohm’s Law

- Voltage
- Sample Area

\[ \rho(t) = \frac{V(t) \cdot A}{I(t) \cdot L} \]

- Resistance
- Current
- Sample Thickness

Measurement limit of \(~0.2\) fA at \(~900\) V with \(2\) cm\(^2\) area and \(25\) µm thick sample
DC Conductivity

- Transient conductivity in constant voltage conductivity tests exhibit the same behavior as photoconductivity

\[
\sigma(t) = \sigma_p \frac{-t}{\tau_p} + \left\{ \sigma_{disp} t^{-(1-\alpha)} \theta(\tau_{transit} - t) + \sigma_{trans} t^{-(1+\alpha)} \theta(t - \tau_{transit}) \right\} + \sigma_{DC}
\]  

(Wood, 2018)
Previous Resistivity Tests

- Data to the left shows the change in resistivity with temperature previously taken with the CVC chamber.
- The change in resistivity occurs around 270 K:
  - transition from multiple trapping to variable range hopping.
- Current tests are shown as conductivity instead of resistivity having a relationship of
  \[ \sigma = \frac{1}{\rho} \]

(Dennison, 2008; Brunson, 2007)
CVC Temperature Runs

**Hot Temperature Run**

- Temperature steps of ~8 °C were taken from room temperature to ~57 °C and then back down
- Each step was allowed to come close to an equilibrium over several hours

**Cold Temperature Run**

- Temperature steps again of ~8 °C were taken from room temperature down to ~-12 °C
- These steps had more uncertainty in the conductivity measurements due to instrumentation behavior at cold temperatures as opposed to hot temperatures
Temperature Results

- A change in slope is expected around 270 K
- This may or may not be evident from seeing a small change in slope but more data is needed below the temperature threshold to claim this with any certainty
Conclusions

• CVC measurements of LDPE have been done from ~260-330 K
• This did not show any clear transition from multiple trapping to variable range hopping
• New data is higher quality with better temperature regulation but (for now) over a smaller range

Future Work

• Data is currently being taken again of LDPE using the CVC system at temperatures lower than those shown previously
• This will then be repeated to create a large set of data to fit the model with more accuracy
References