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Charge Transport in Disordered Materials and the Dispersion Parameter

Zachary Gibson
Utah State University

Charge Transport in Disordered Materials and the Dispersion Parameter

Zack Gibson

Utah State University Colloquium

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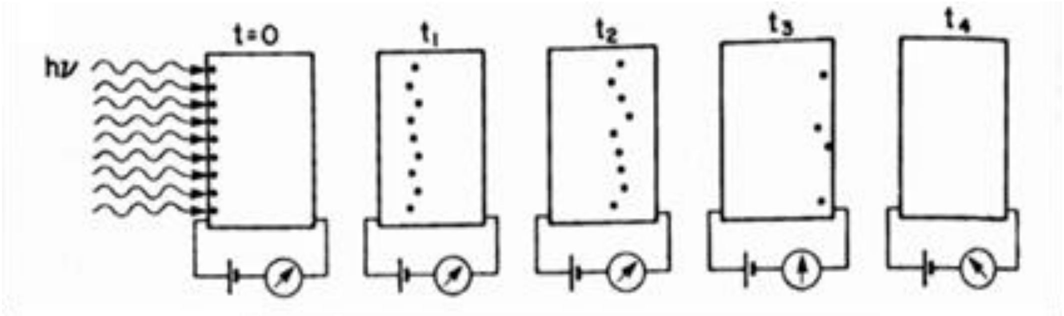
Outline

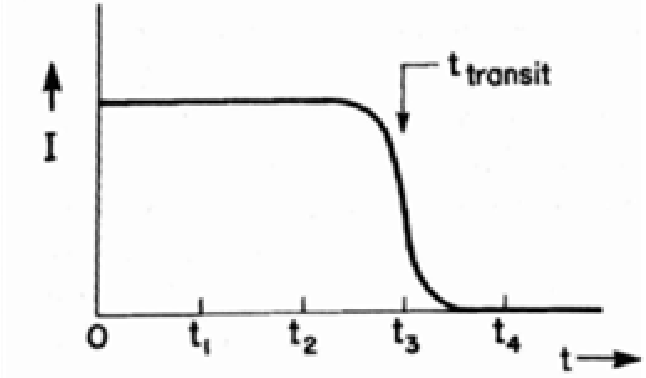
- Motivation
- Conduction in Crystalline Solids
- Localization
  - Defects
- Conduction in Disordered Solids
- Modeling of Charge Transport in Disordered Solids
  - Transients
  - Steady State
- The Dispersion Parameter
  - Equations and physical interpretation
  - Dispersive to normal transport transitions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

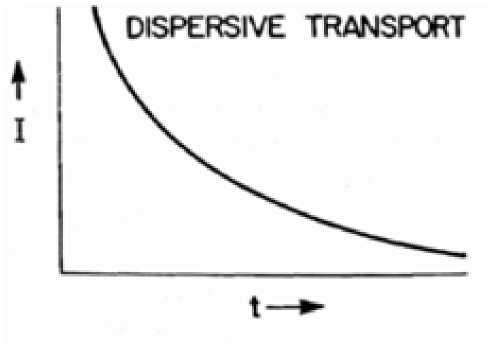
Why?

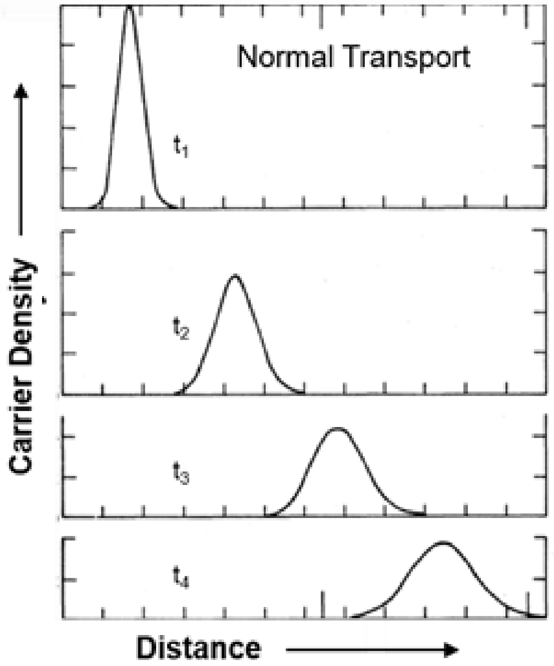


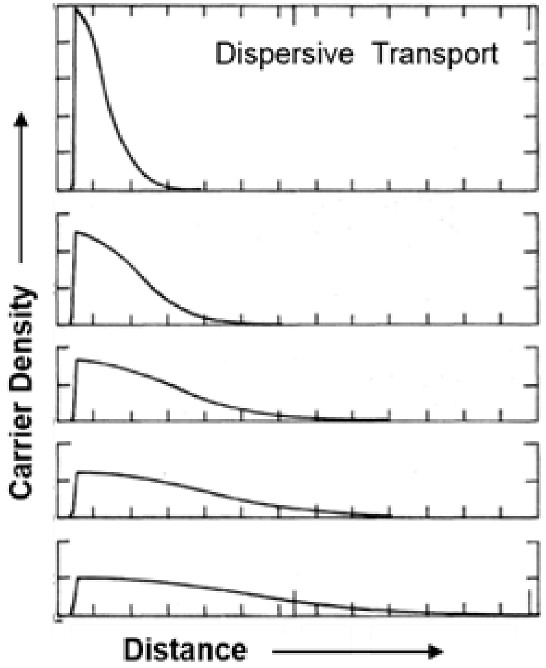
- Connect microscopic processes to macroscopic behavior
- Explain anomalous/dispersive behavior
- Theory has applications from spacecraft charging to HVDC cable insulation
- Defines many different material properties and measurements characteristics

$$\alpha(T) = \frac{kT}{E_c} = \frac{T}{T_c} \qquad \alpha(E) = \frac{qaE}{2kT_c}$$







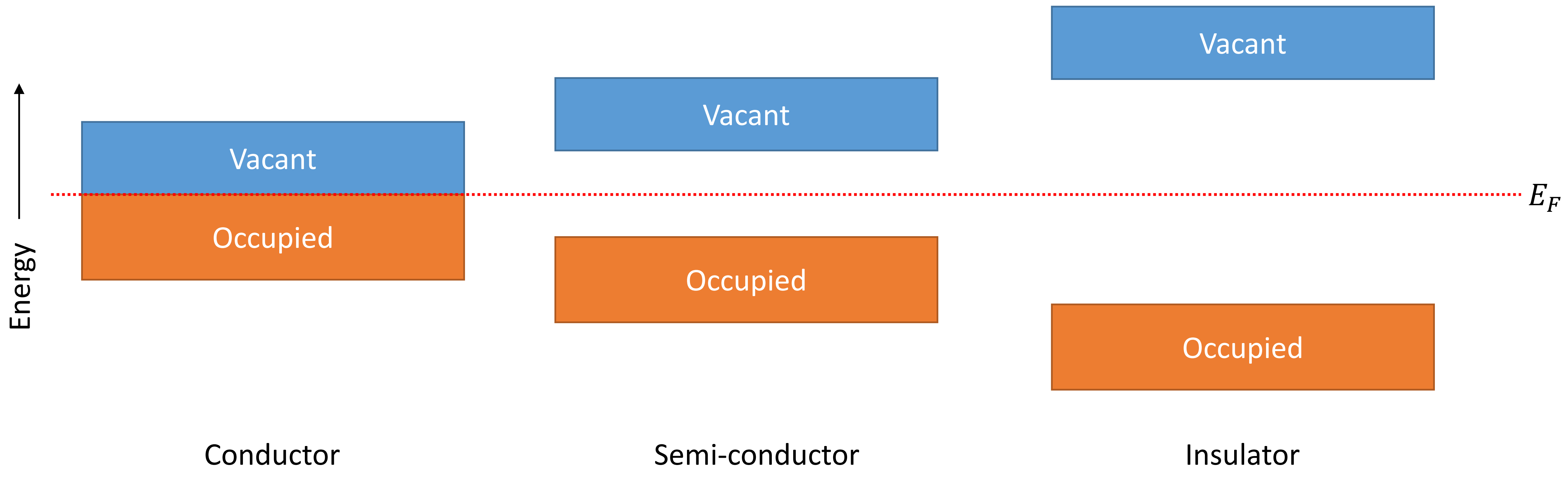


(Zallen, 1983)

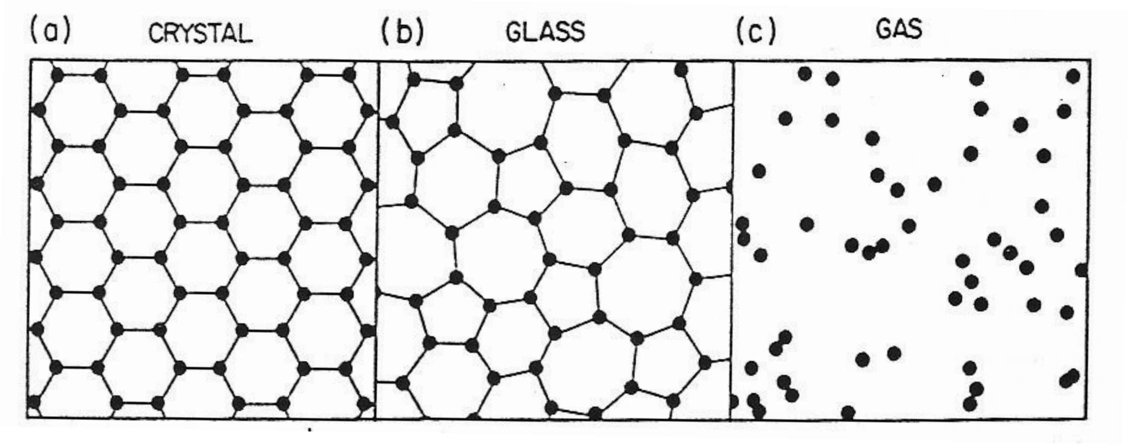
Understanding Conduction - Crystalline

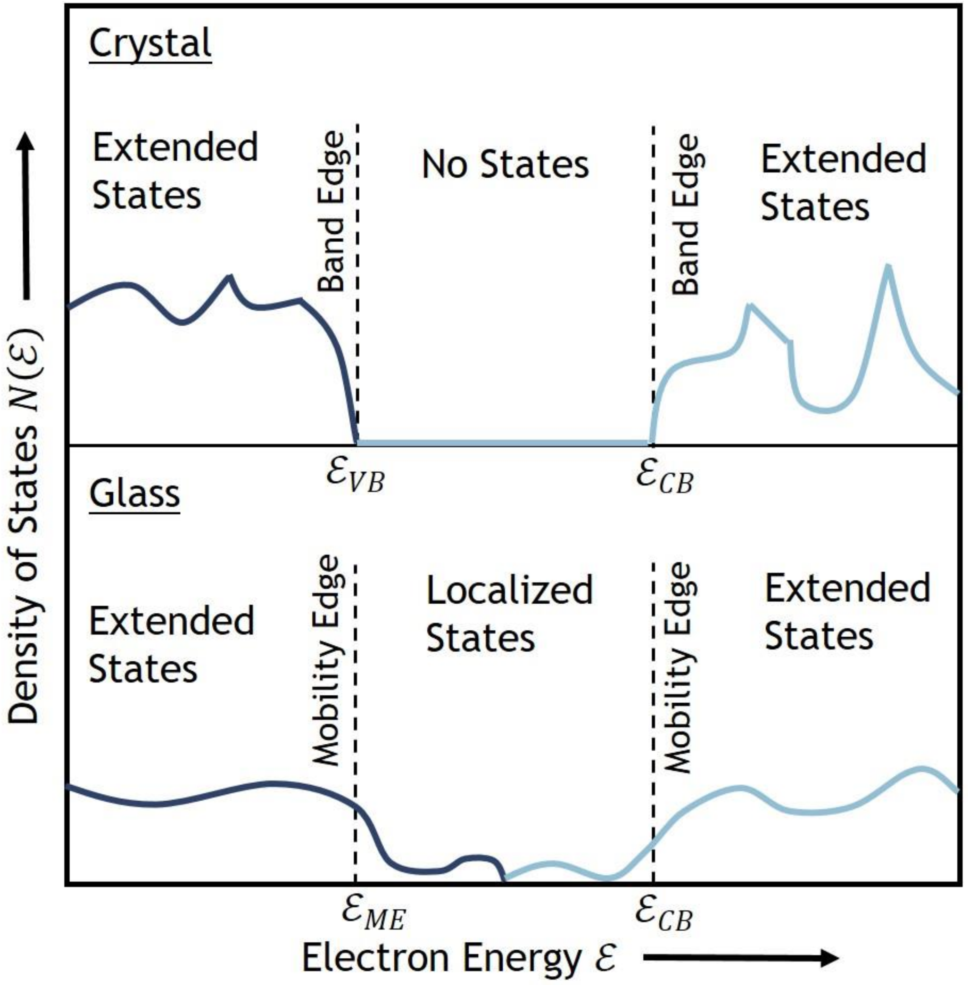
- Perfect periodic structure (long-range order)

Schrödinger′s Equation $\frac{-\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) + V(\boldsymbol{r})\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$ $\longrightarrow$ Bloch Functions $\psi_k(r) = u_k(\boldsymbol{r})\mathrm{e}^{\boldsymbol{ik\cdot r}}$



Understanding Conduction - Amorphous





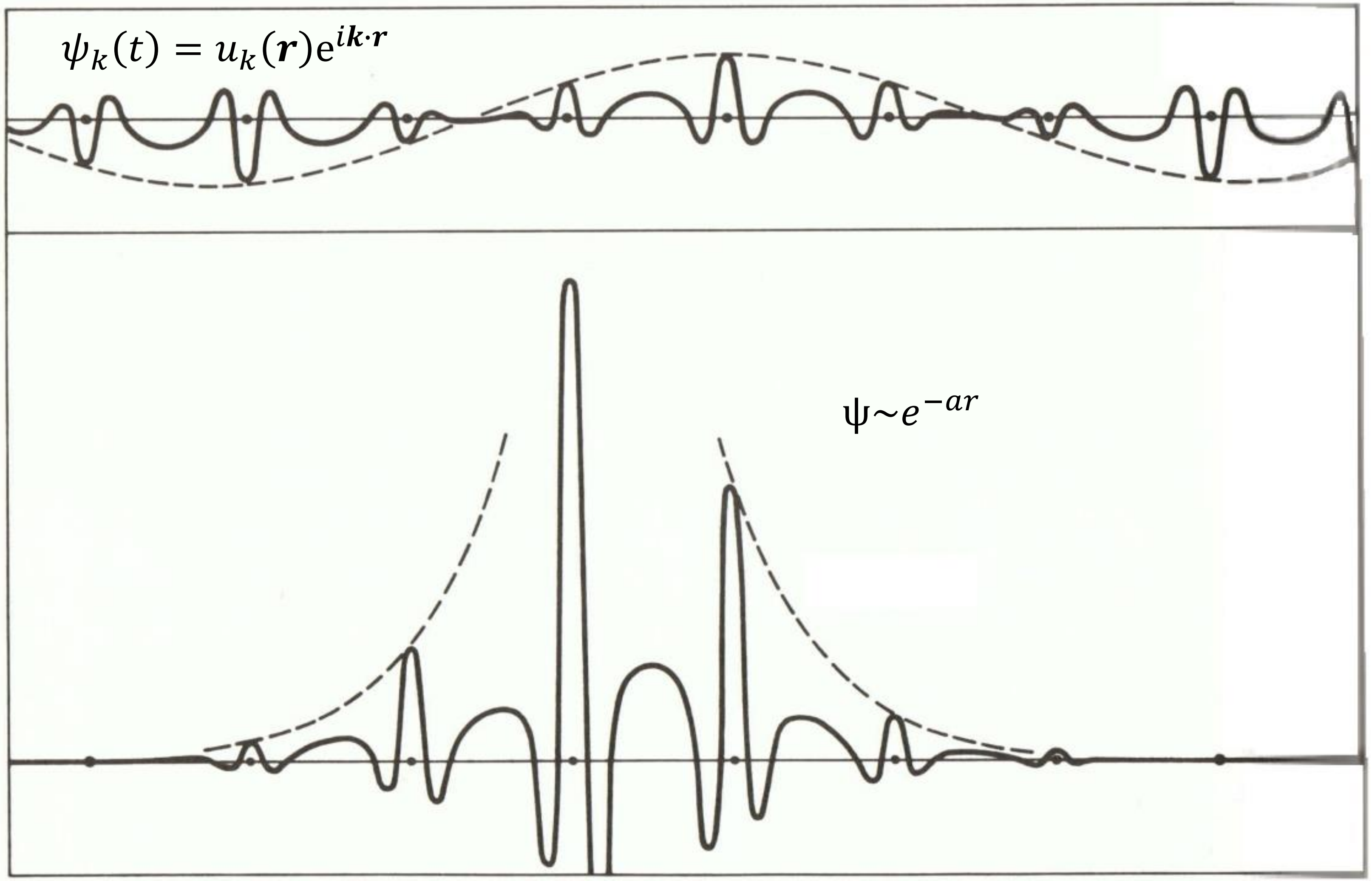
Amorphous solids exhibit

- No long-range order
- Short-range order
- Atoms have equilibrium point

(Zallen, 1983)

Understanding Conduction - Localization

- Extended state wavefunction
- Localized wavefunction

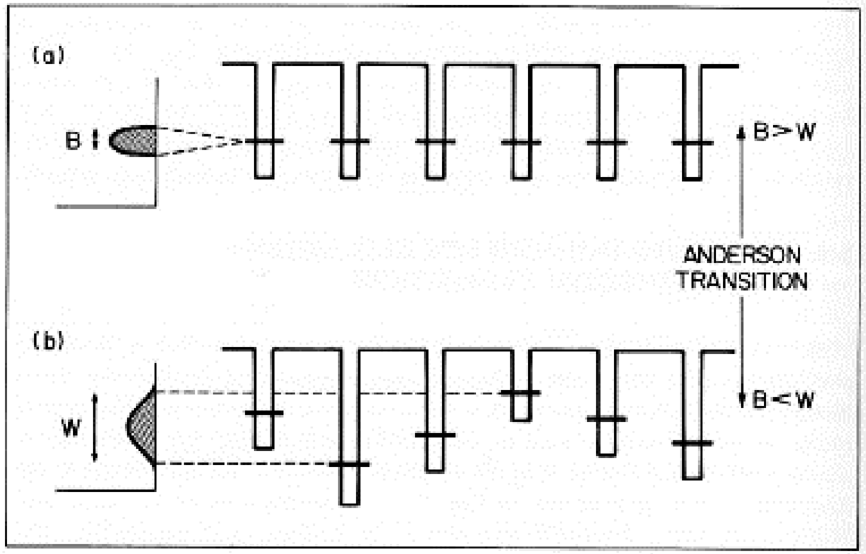


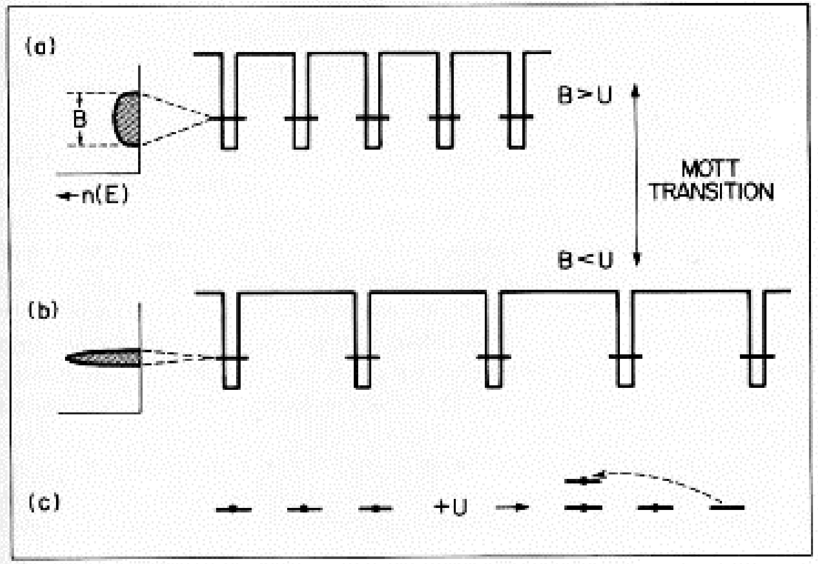
(Zallen, 1983)

Understanding Conduction - Localization

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

Transition	*Electron Wave Functions* Metal side of Transition	Insulator side of Transition	Characteristic Energies	Change at the $M \rightarrow I$ Transition	Criterion for Localization
Bloch	Extended	Extended	Bandwidth B	Partly filled bands → all bands filled or empty	—
Mott	Extended	Localized	Electron–electron (e^2/r_{ij}) correlation energy U	Correlation-induced localization	$U > B$
Anderson	Extended	Localized	Width W of the distribution of random site energies	Disorder-induced localization	$W > B$



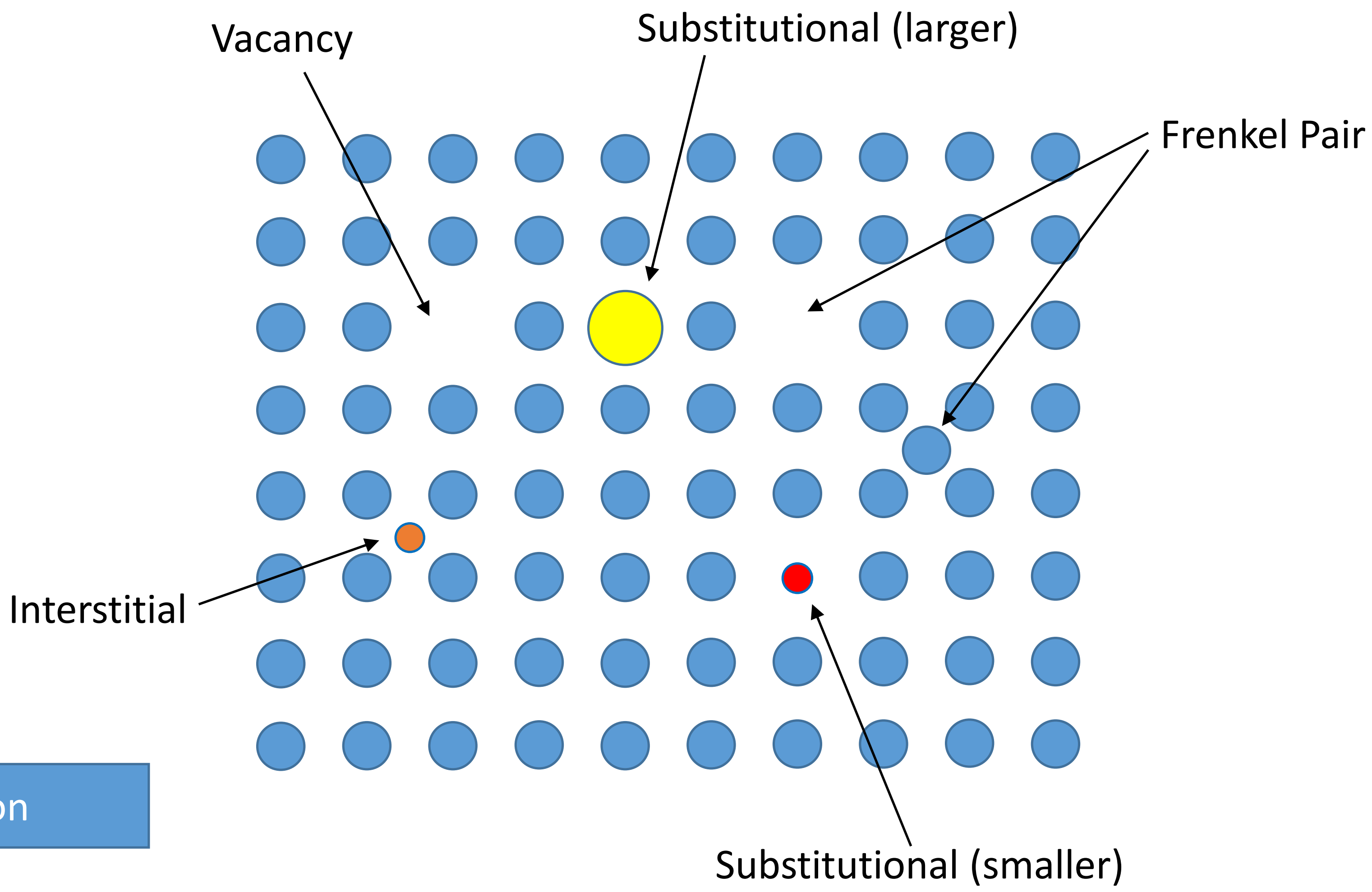


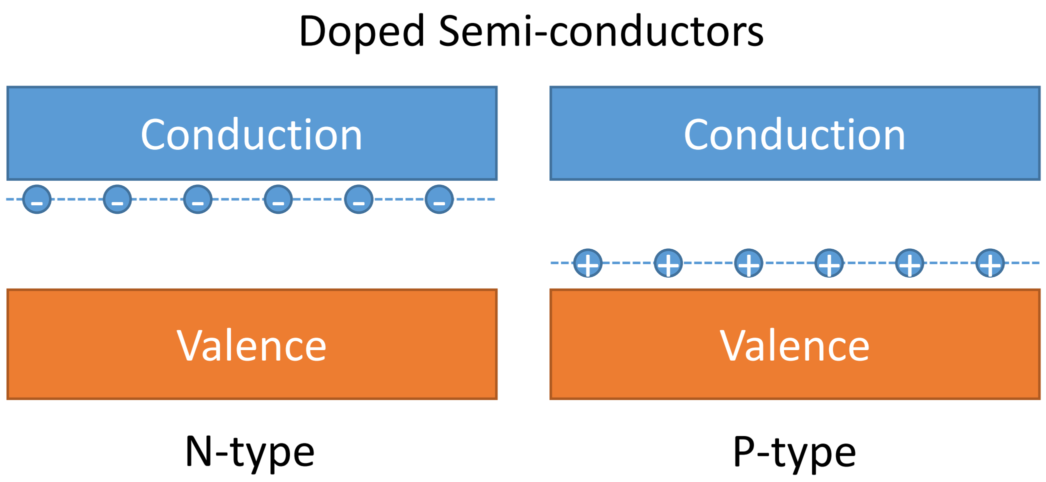
(Zallen, 1983)

Defects

Types of Defects:

- Point
- Line (1D)
- Planar (2D)
- Volume (3D)

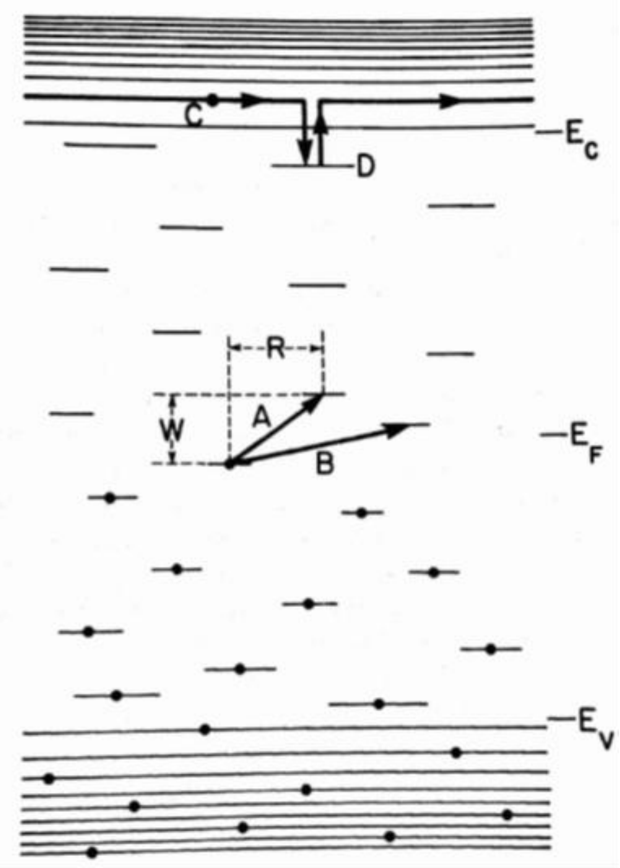




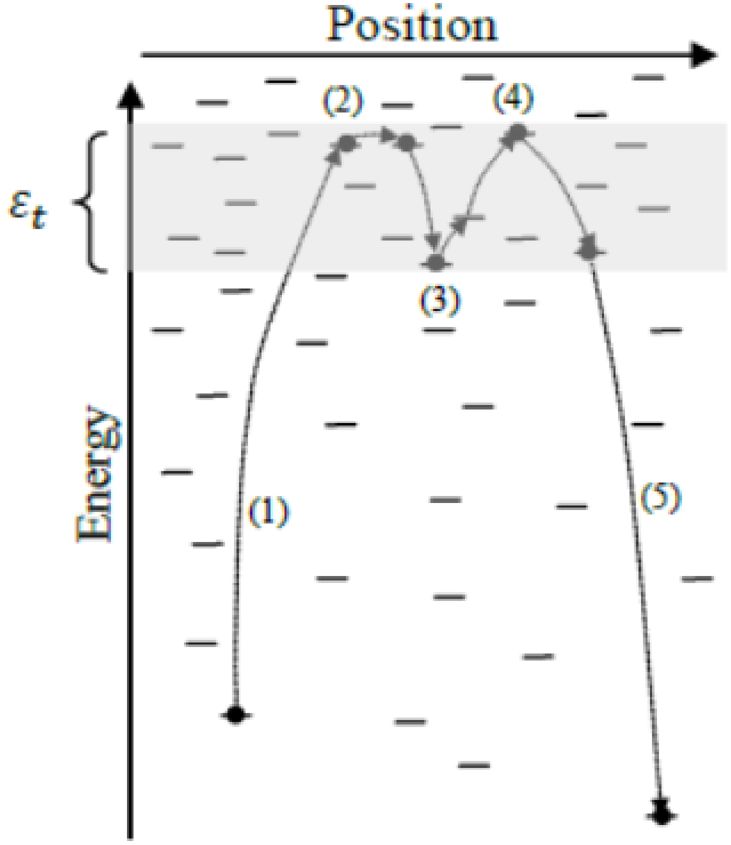
Understanding Conducting - Amorphous

Conduction mechanisms in amorphous insulators:

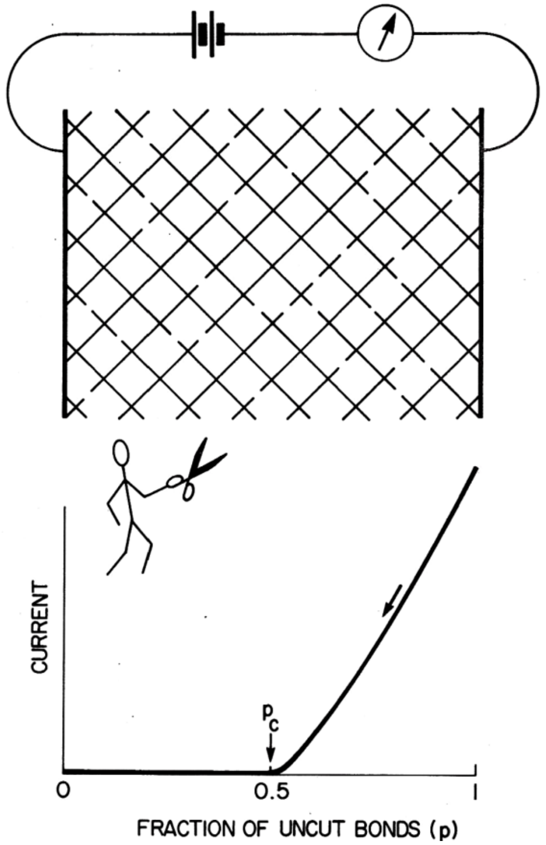
Multiple Trapping and Thermally Assisted Hopping



Variable Range Hopping and Radiation Induced Conductivity

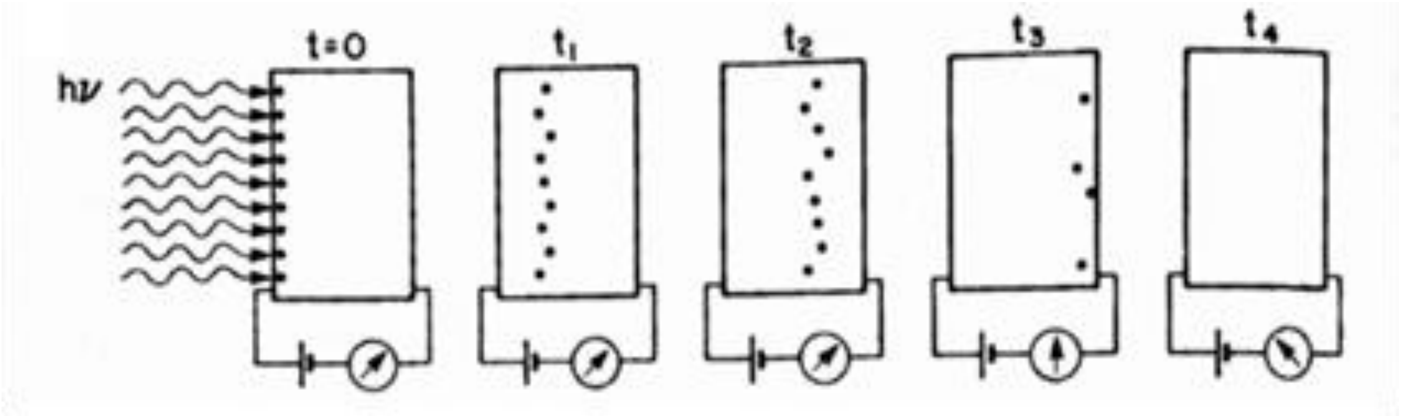


Percolation

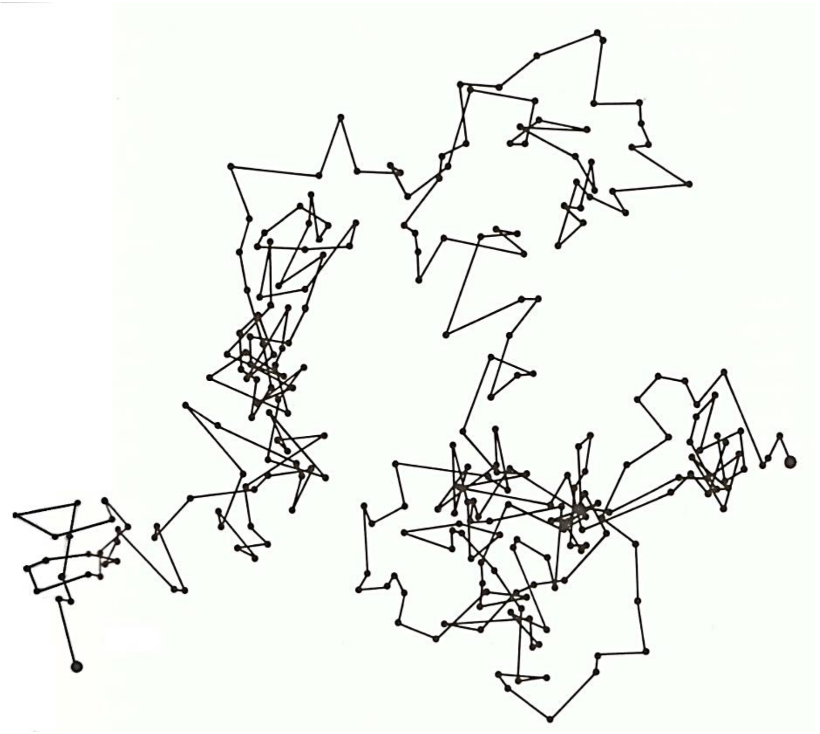


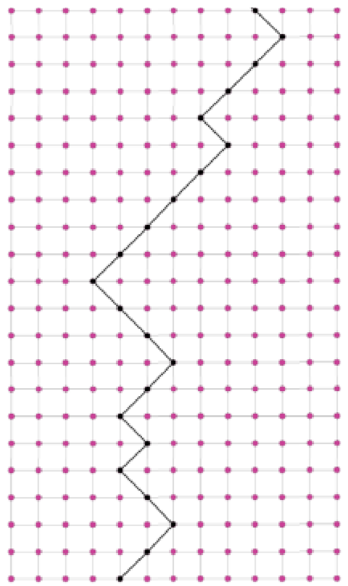
(Zallen, 1983; Sim 2013)

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

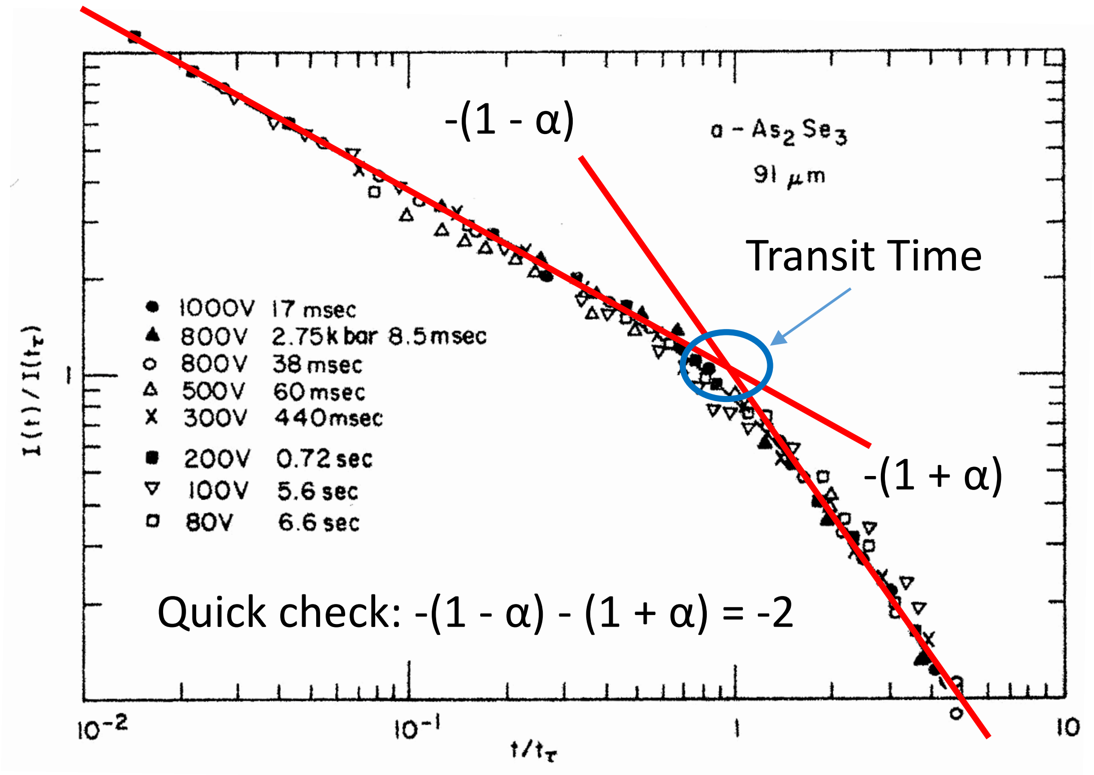




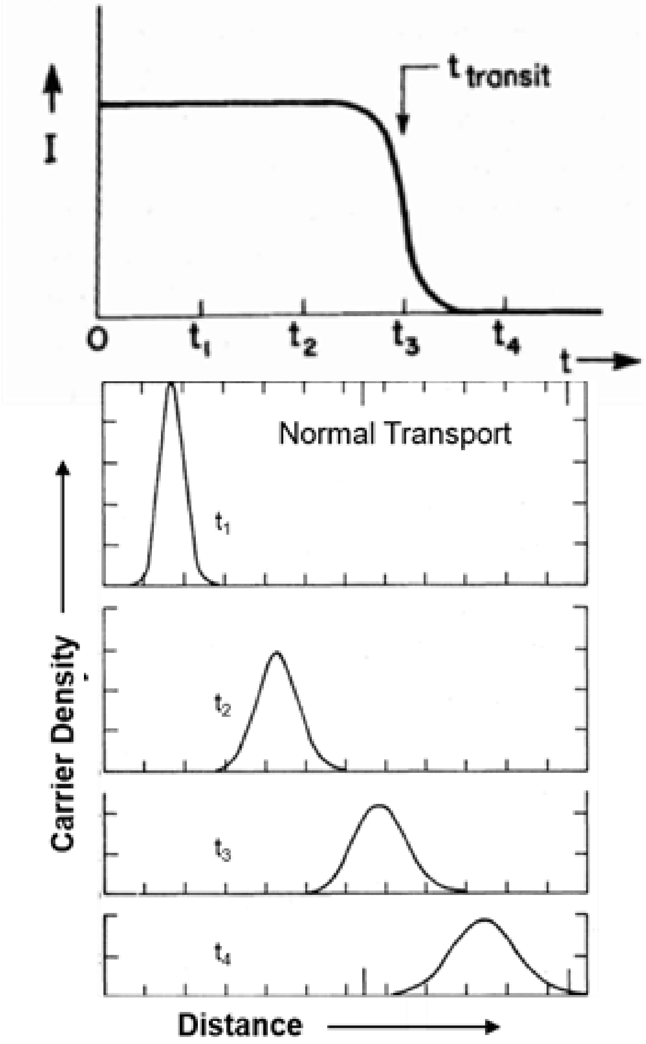
(Gillespie, 2017; Zallen, 1983)

Transient Anomalous Phenomena - Photoconductivity

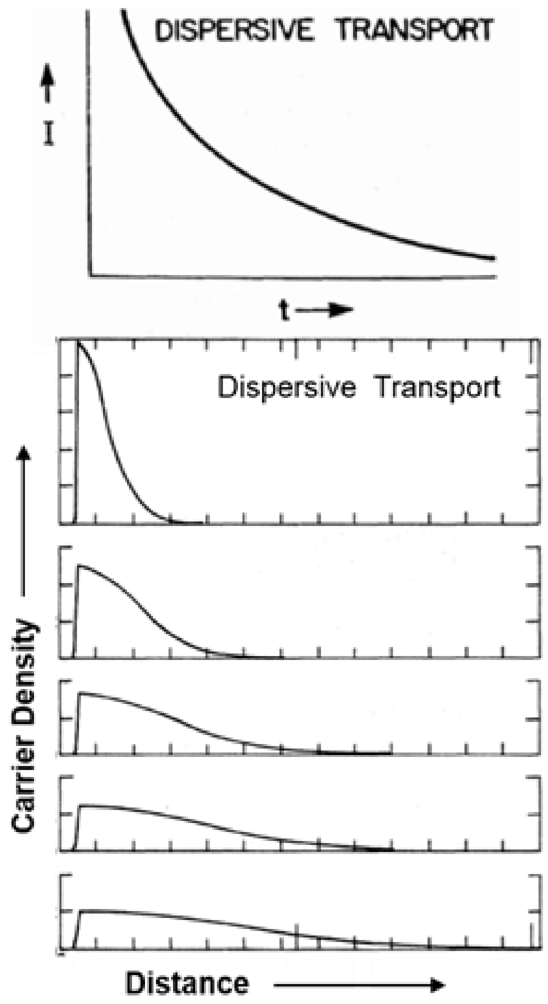
$$I(t) \sim \begin{cases} \frac{1}{\Gamma(\alpha) t^{1-\alpha}} & t \ll t_{transit} \\ \frac{1}{-\Gamma(-\alpha) t^{1+\alpha}} & t \gg t_{transit} \end{cases}$$



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



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

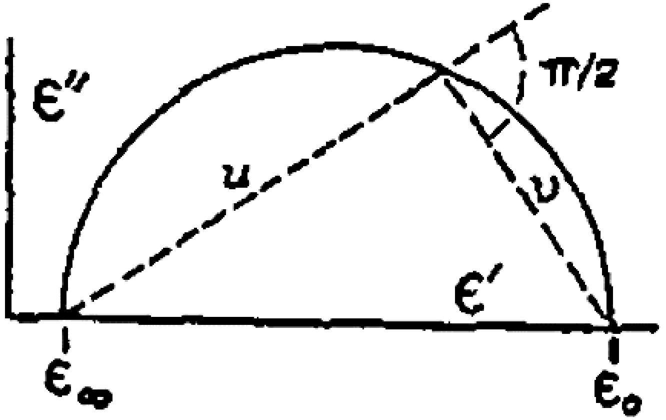


(Zallen, 1983; Scher, 1975)

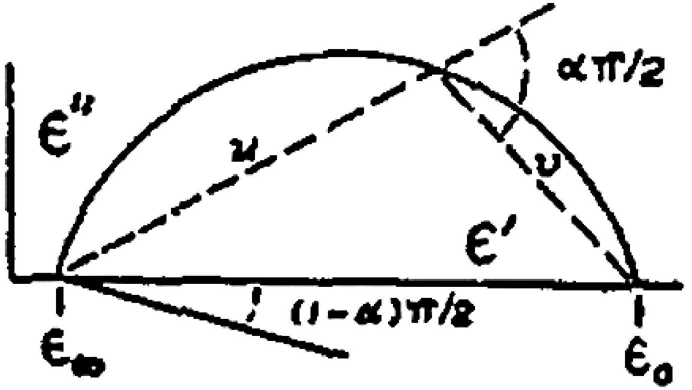
Transient Anomalous Phenomena – Permittivity and Conductivity

- 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

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



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

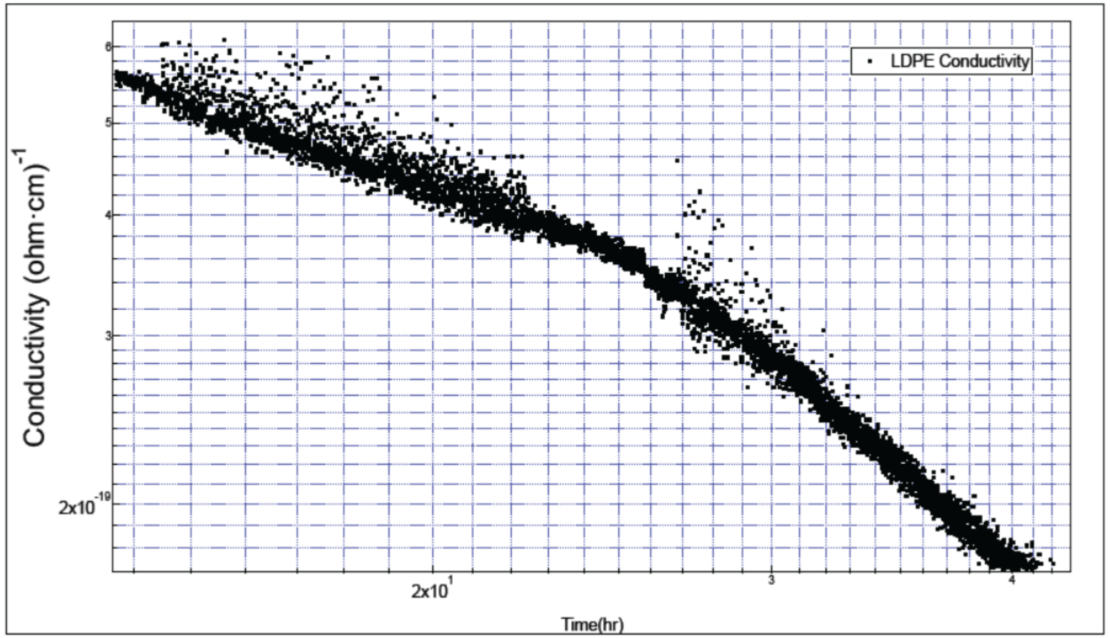


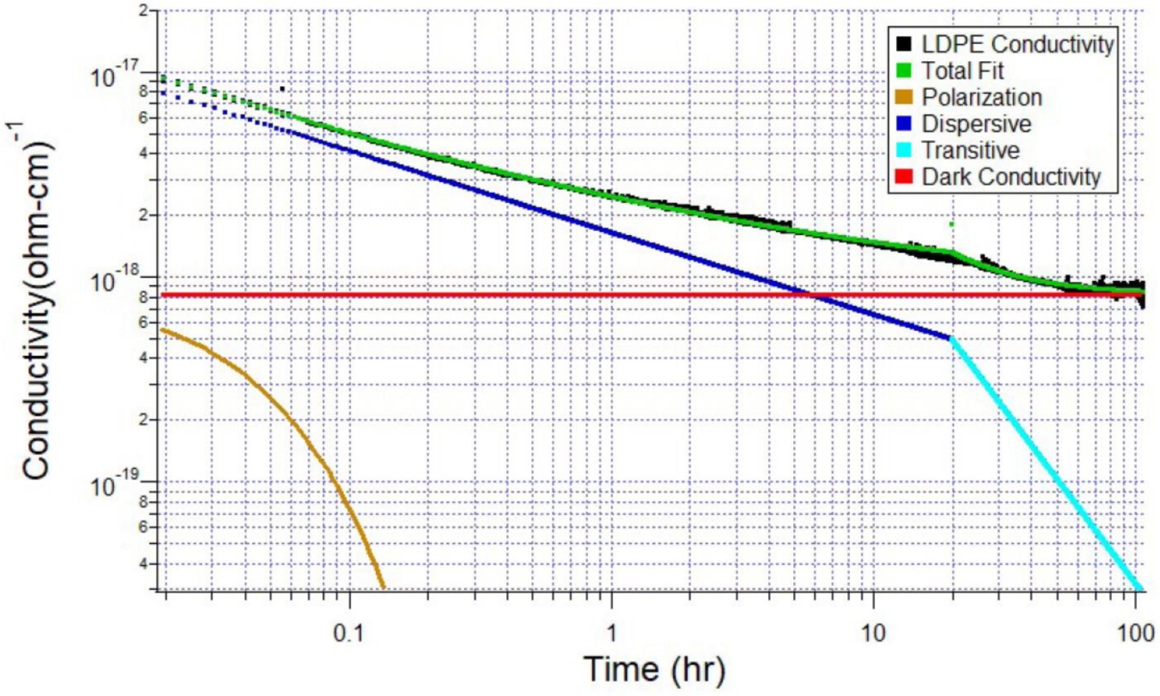
$$I(t) = \begin{cases} \dfrac{\varepsilon_0 - \varepsilon_\infty}{\tau_0} \dfrac{1}{\Gamma(\alpha)} \left(\dfrac{t}{\tau_0}\right)^{-(1-\alpha)} & t \ll t_{transit} \\ \dfrac{\varepsilon_0 - \varepsilon_\infty}{\tau_0} \dfrac{(-1)}{\Gamma(\alpha)} \left(\dfrac{t}{\tau_0}\right)^{-(1+\alpha)} & t \gg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

(Cole, 1941)

Transient Anomalous Phenomena – Permittivity and Conductivity

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





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

(Wood, 2018)

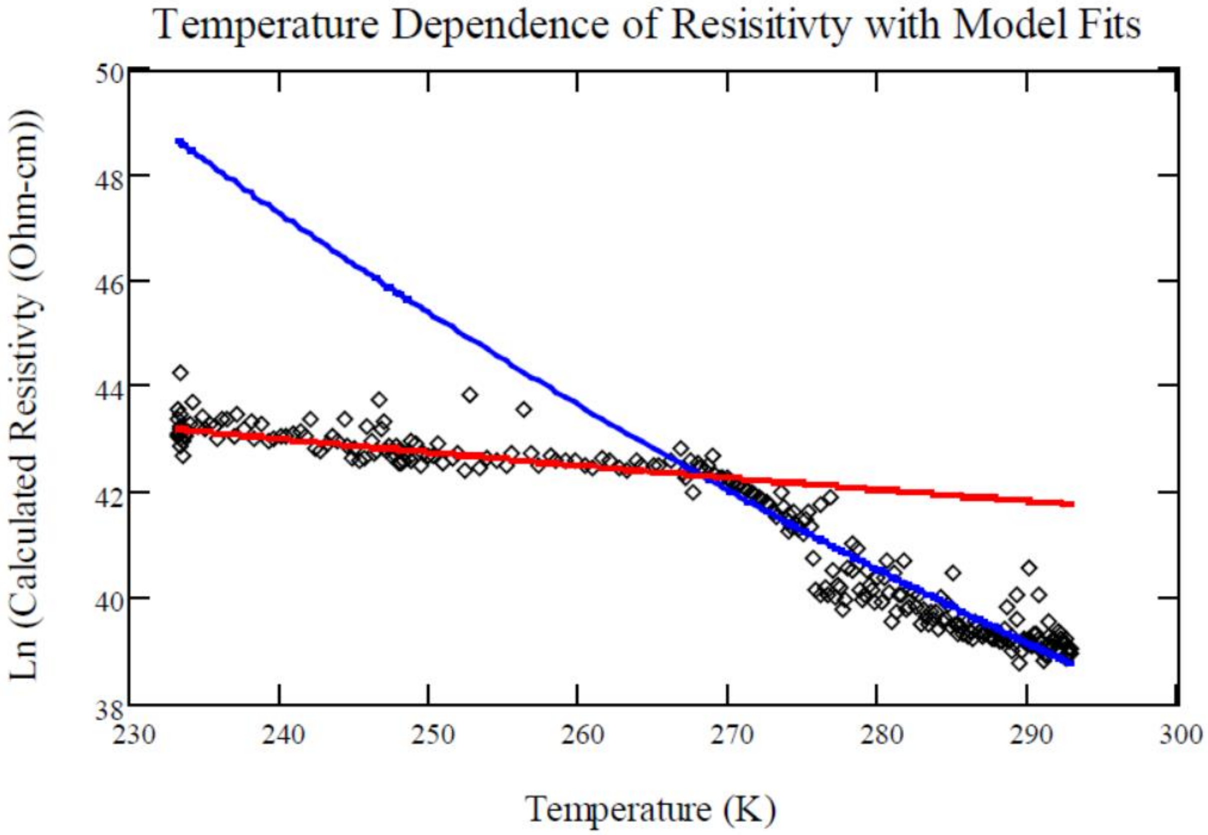
Steady State Phenomena – DC Conductivity

Two regimes:

- Assuming low applied field

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

$$\alpha(T) = \frac{T}{T_c}$$



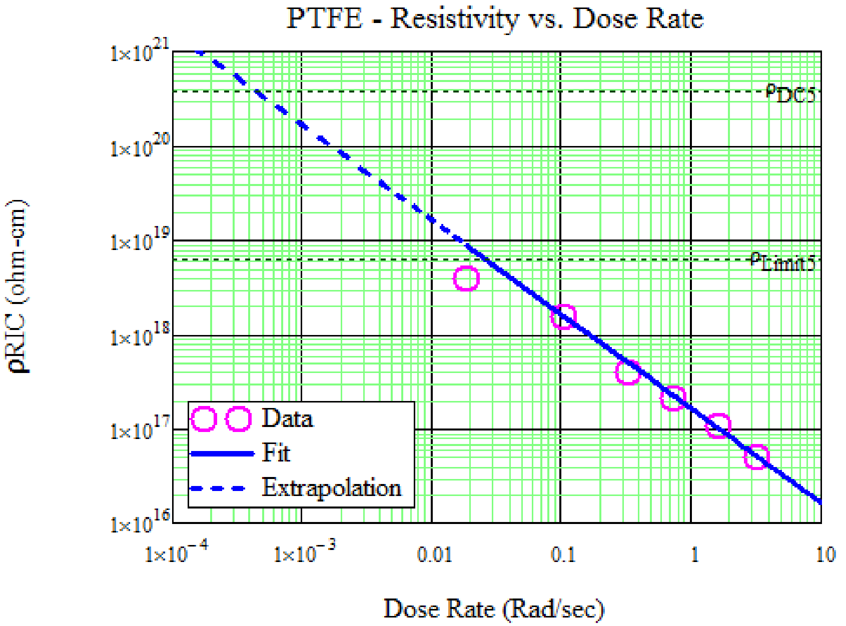
(Dennison, 2008; Brunson, 2007)

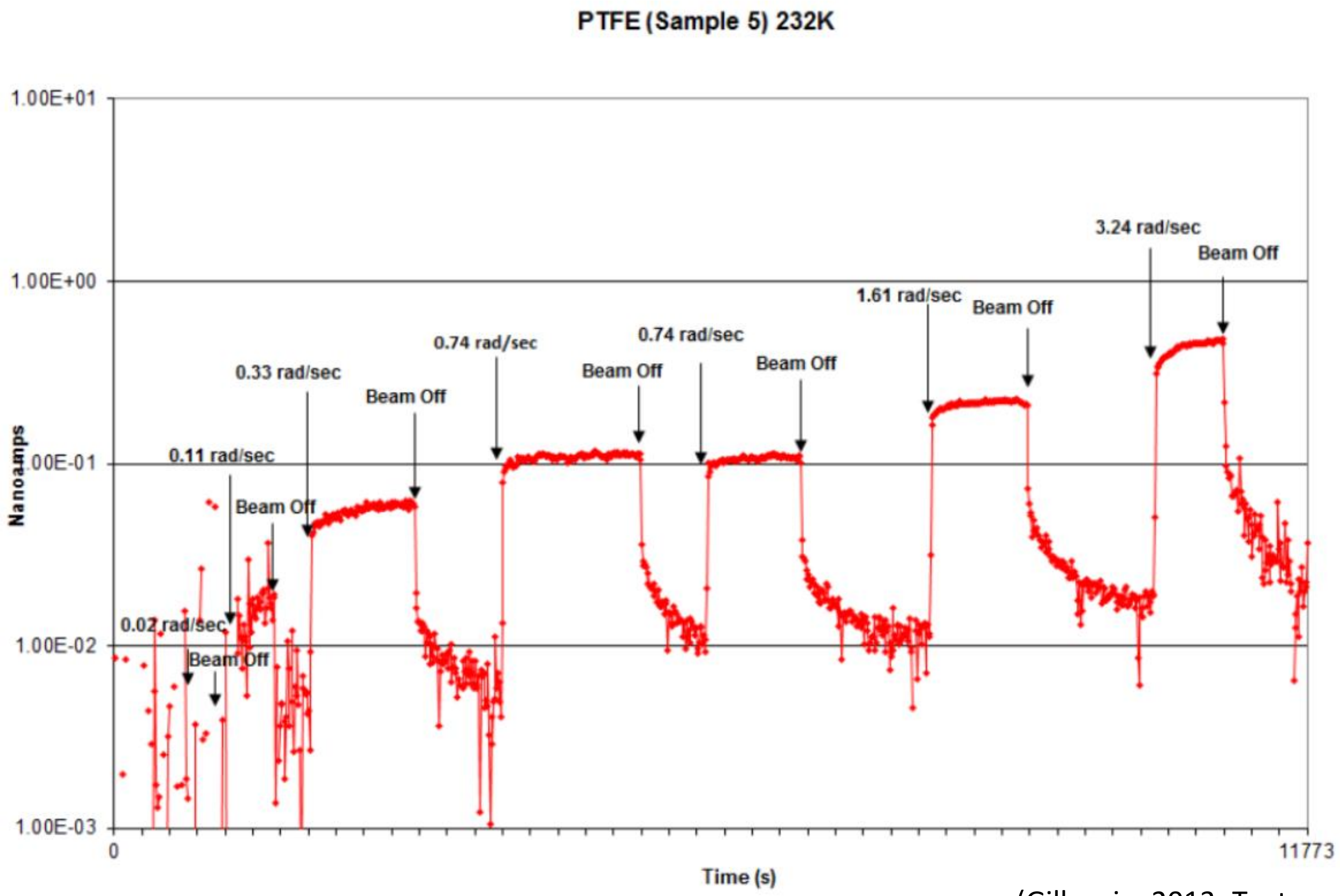
Steady State Phenomena – Radiation Induced Conductivity

- Radiation induced conductivity is also defined by the dispersion parameter

$$\sigma_{RIC} = k_{RIC}(T)\dot{D}^{\Delta}$$

$$\Delta = \frac{T_c}{T_c + T} = \frac{1}{1 + \frac{T}{T_c}} = \frac{1}{1 + \alpha}$$





(Gillespie, 2013; Tyutnev, 2006)

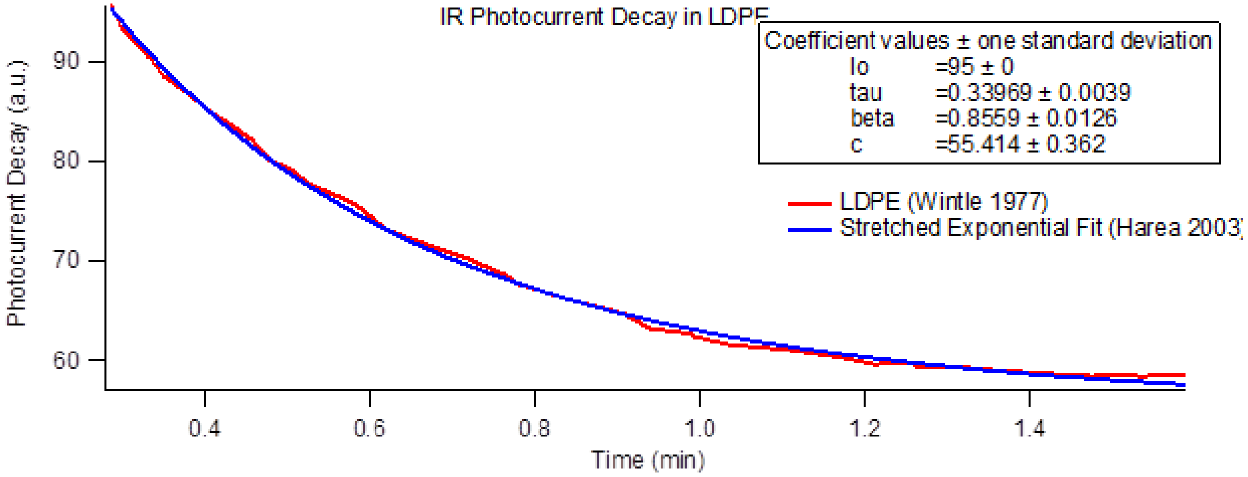
Anomalous Phenomena – Other

Experiments:

- Charge decay as modeled with a stretched exponential
  $$I_{ph}(t) = I_{ph}(0)e^{-\left(\frac{t}{\tau}\right)^{\beta}} + constant$$
  - β = 1 – α
- Surface voltage potential
- Luminescence
- Secondary electron yield

Modeling Approaches:

- Fractional dynamic equations
- Effective medium approach



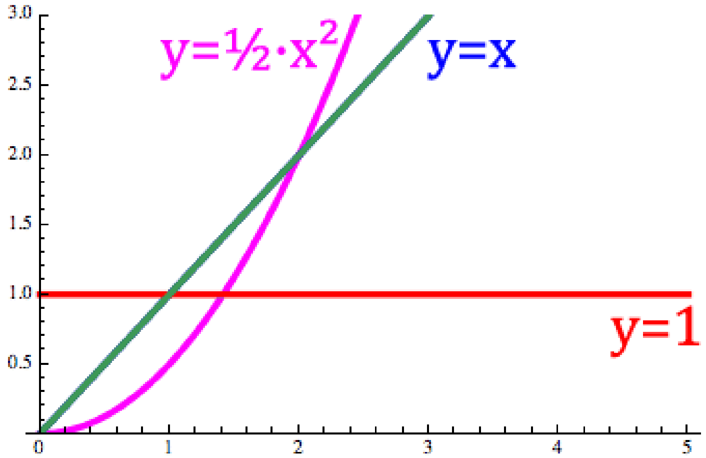
Fractional Diffusion Equation

$$\frac{\partial}{\partial t}P(x,t) = {}_0D_t^{1-\alpha} K_\alpha \frac{\partial^2}{\partial x^2}P(x,t)$$

Fractional Fokker-Planck Equation

$$\frac{\partial P}{\partial t} = {}_0D_t^{1-\alpha}\left(-\frac{\partial}{\partial x}\frac{F(x)}{m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2}\right)P(x,t)$$

Fractional Derivative



(Metzler 2004)

Physical Significance of α

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 → 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."

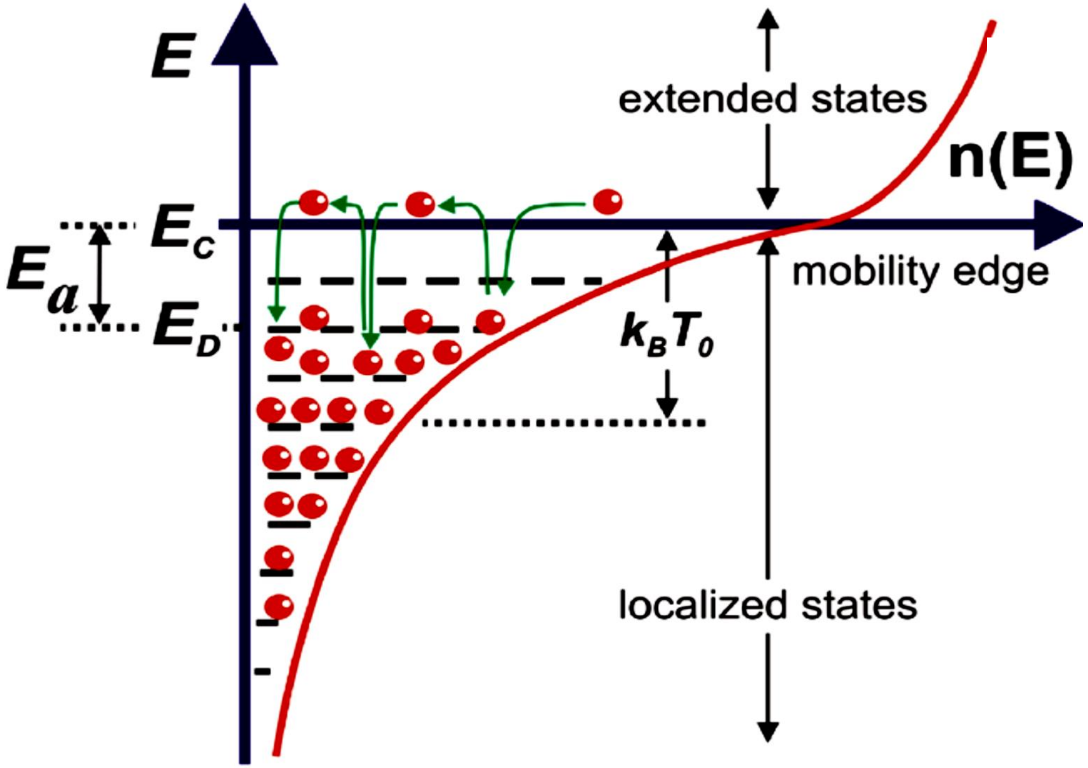
(Pfister, 1978)

To obtain a broad dispersion of transit times (or featureless[11] 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 t_T. This is called the critical trap criterion (CTC).

(Schmidlin 1977)

Density of States - Exponential

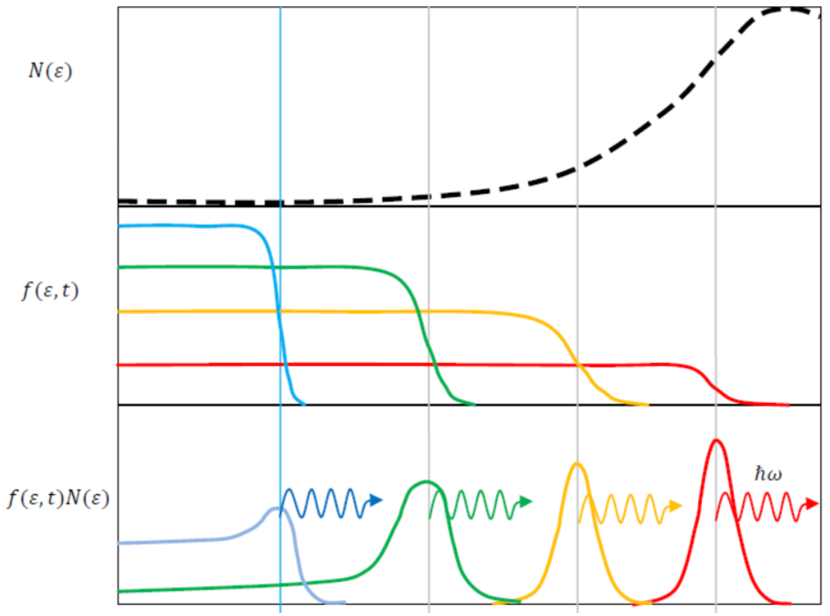
- Exponential energetic density of states in mobility gap
- Most commonly used in the literature
- Otherwise Gaussian is considered
  - Math considerably more complex (often numerical)

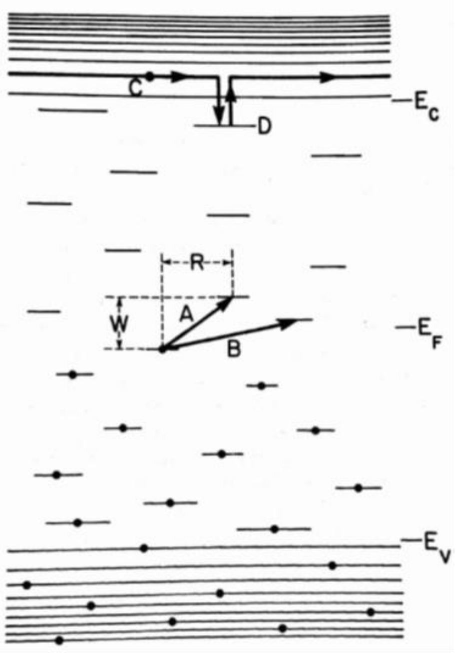


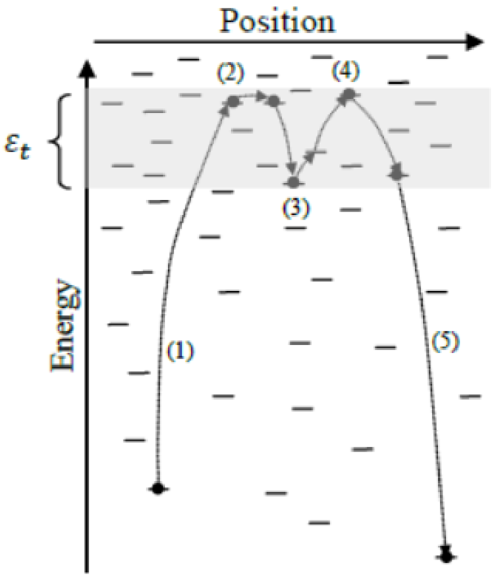
(Adhikari, 2018)

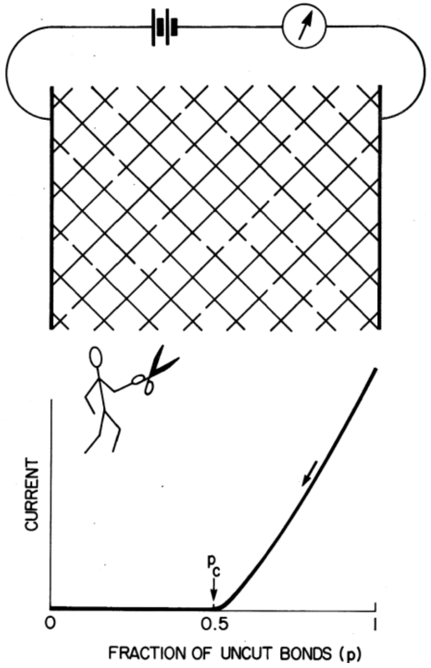
Physical Significance of α

- 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)

Physical Significance of α

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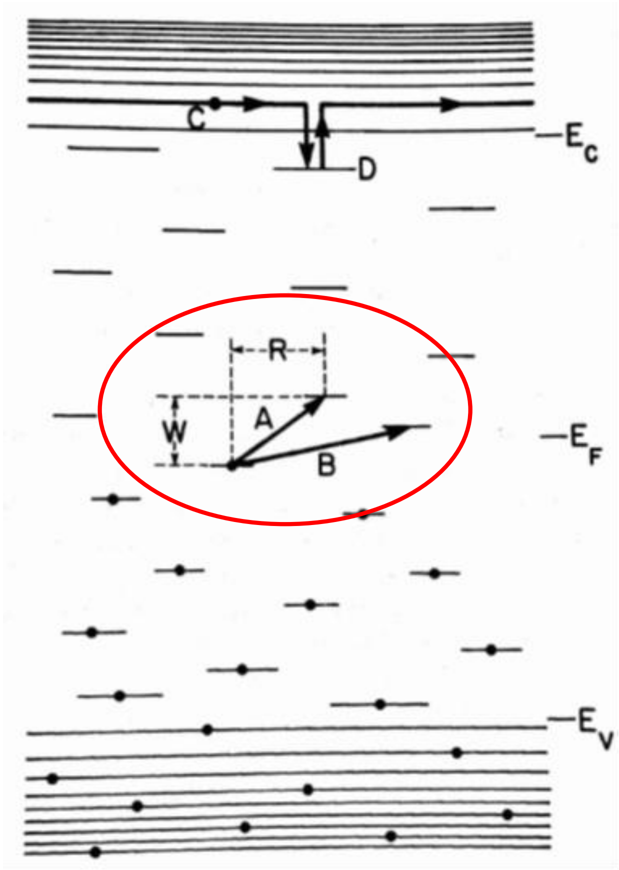

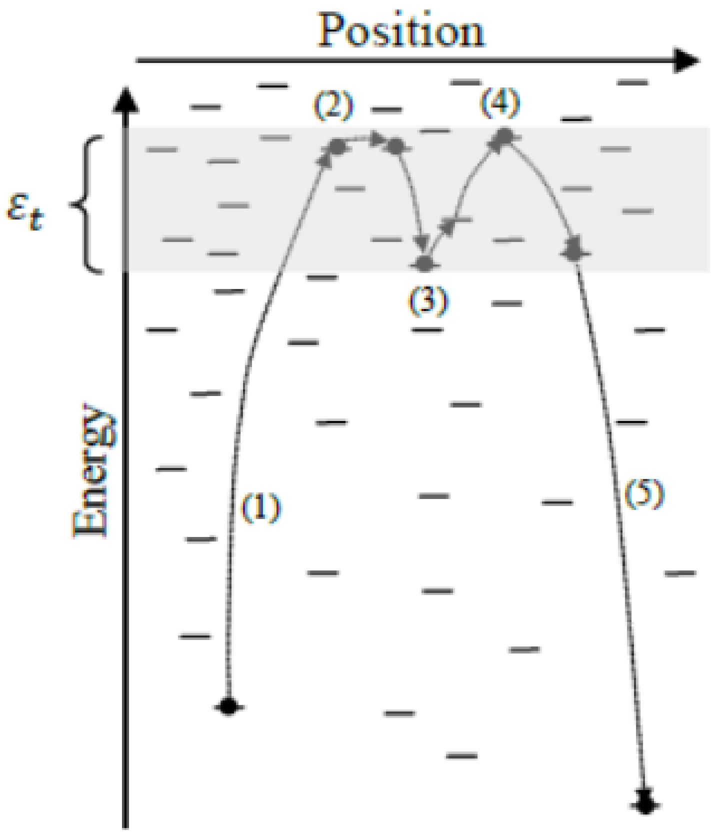

(Zallen, 1983; Sim, 2013)

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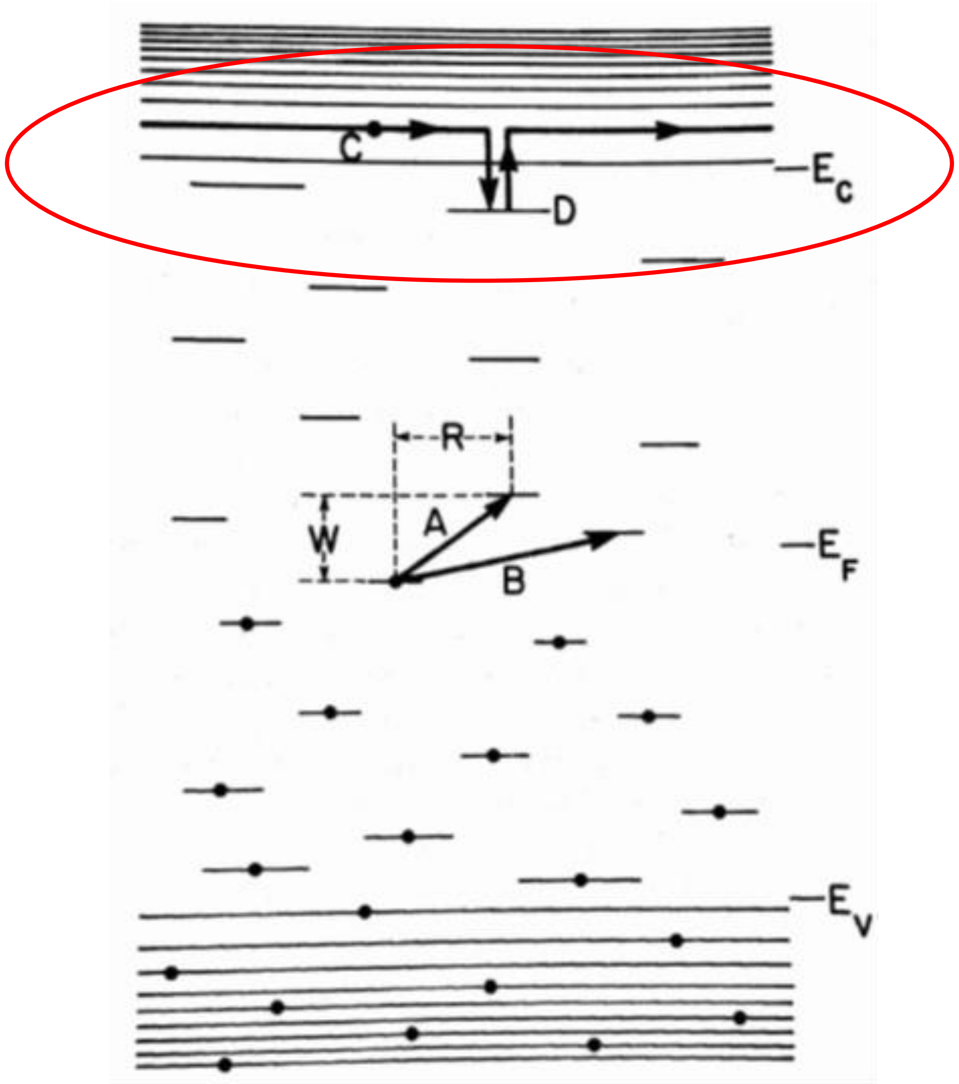

(Zallen, 1983)

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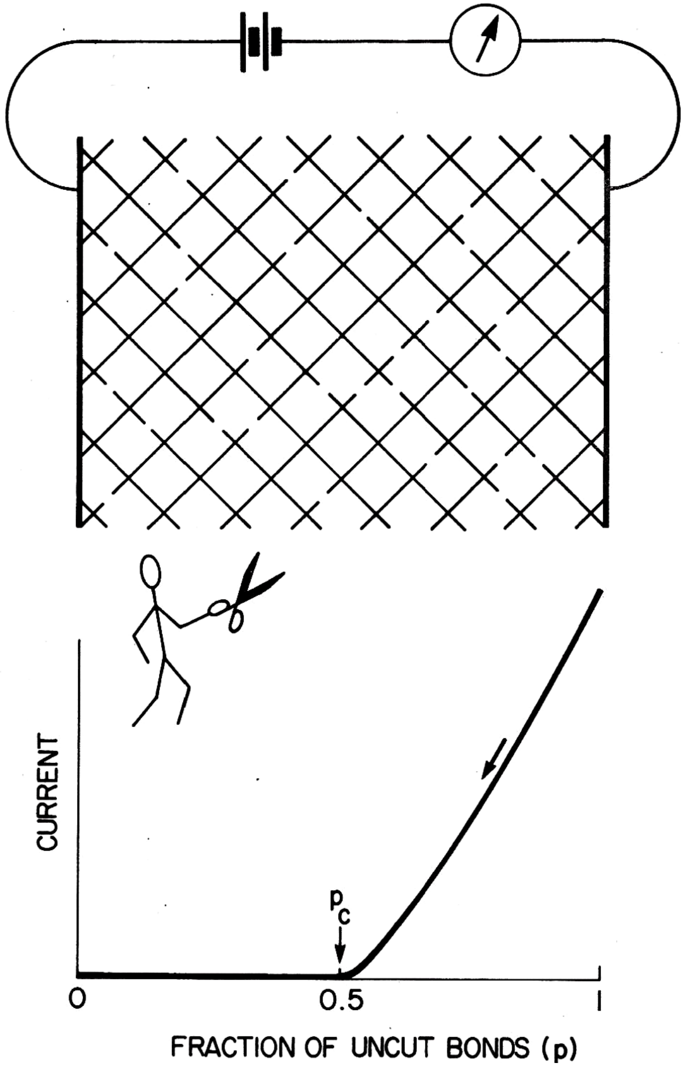

(Zallen, 1983)

(Sim, 2013; Tiedje, 1981)

Physical Significance of α

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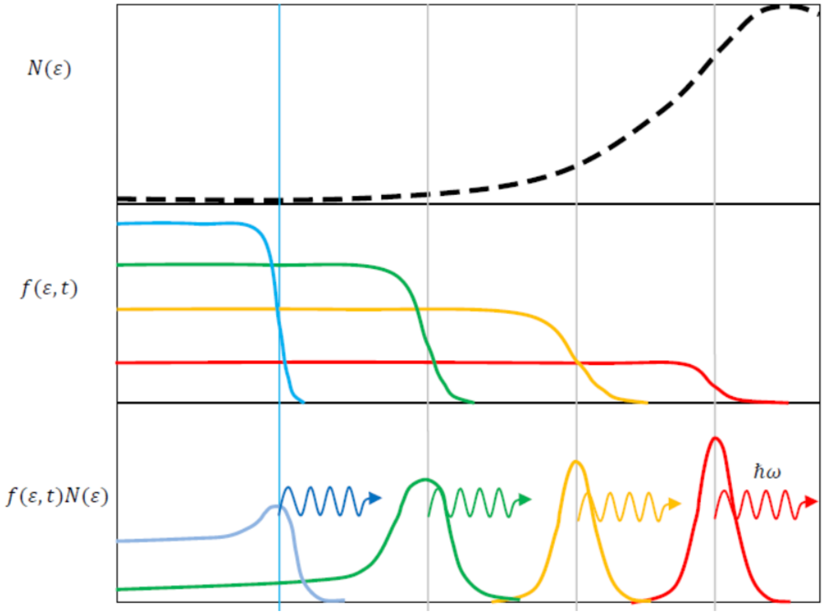


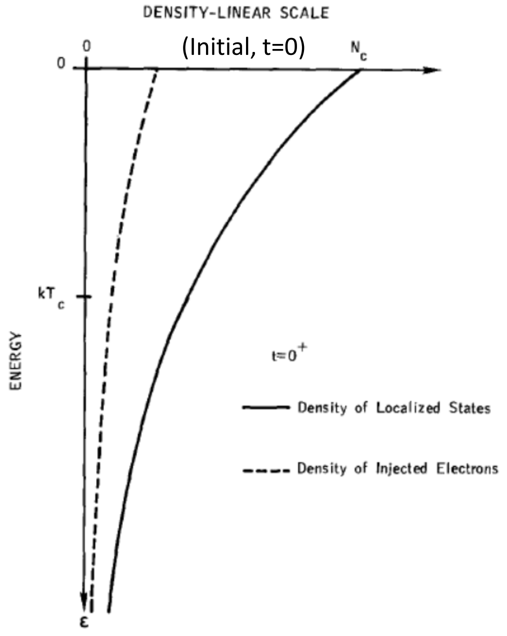


Figure 1 - Distribution of injected electrons in traps after one trapping time, plotted on a linear scale. The zero of energy isthe conduction band mobility edge.

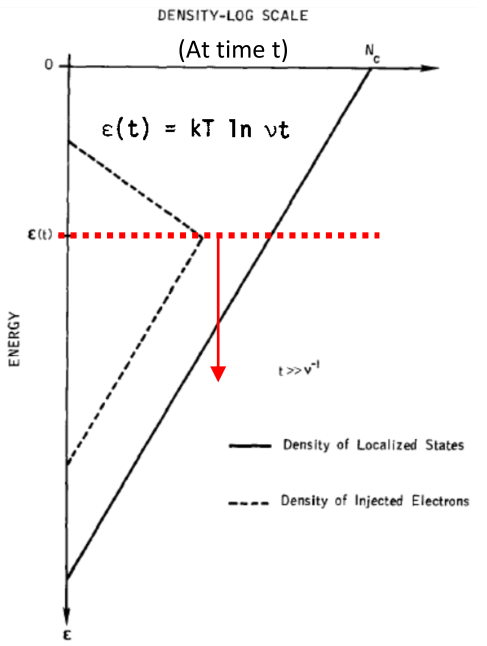
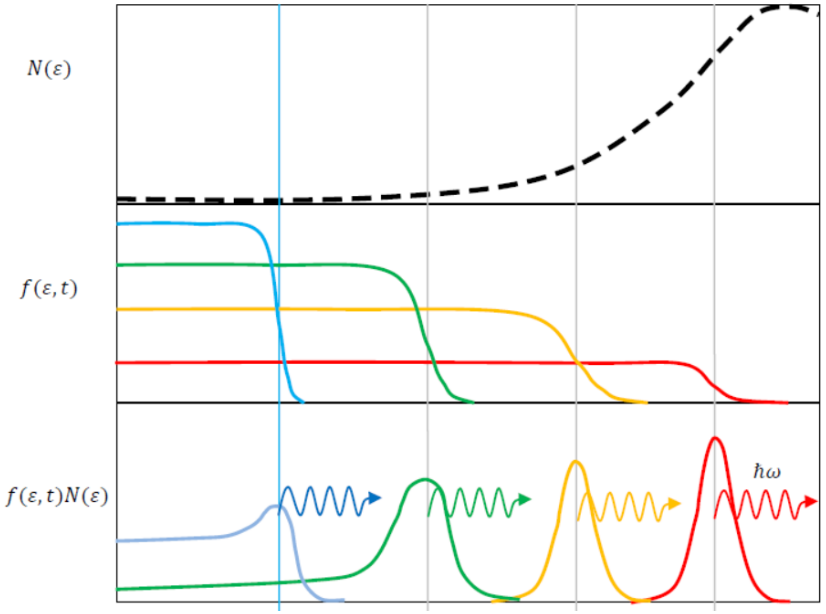


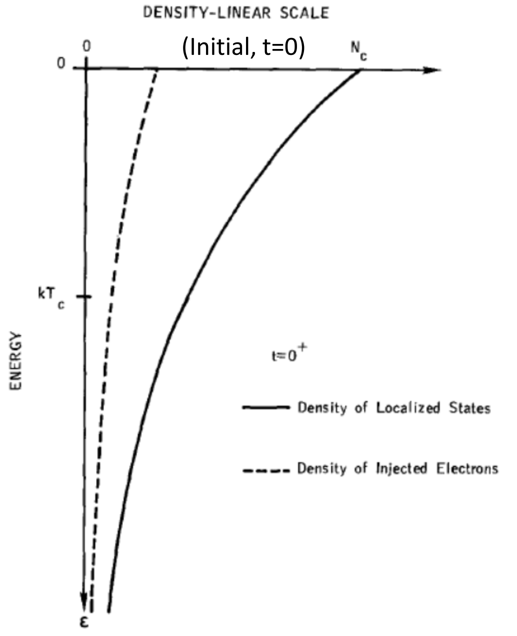
Figure 2 - Distribution of electrons at time t, on a log scale, many trapping times after the injection pulse. In the text the peak in the density at $\varepsilon(t) = kT \ln \nu t$ is treated as being sharp, although in practice it is smoothly rounded

(Sim, 2013; Tiedje, 1981)

Physical Significance of α - 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)





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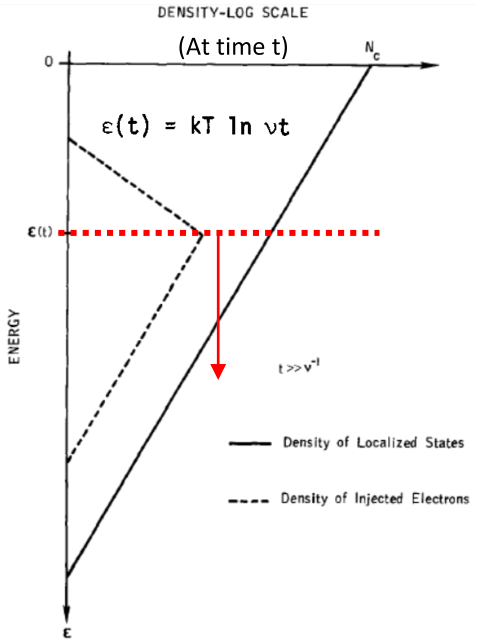

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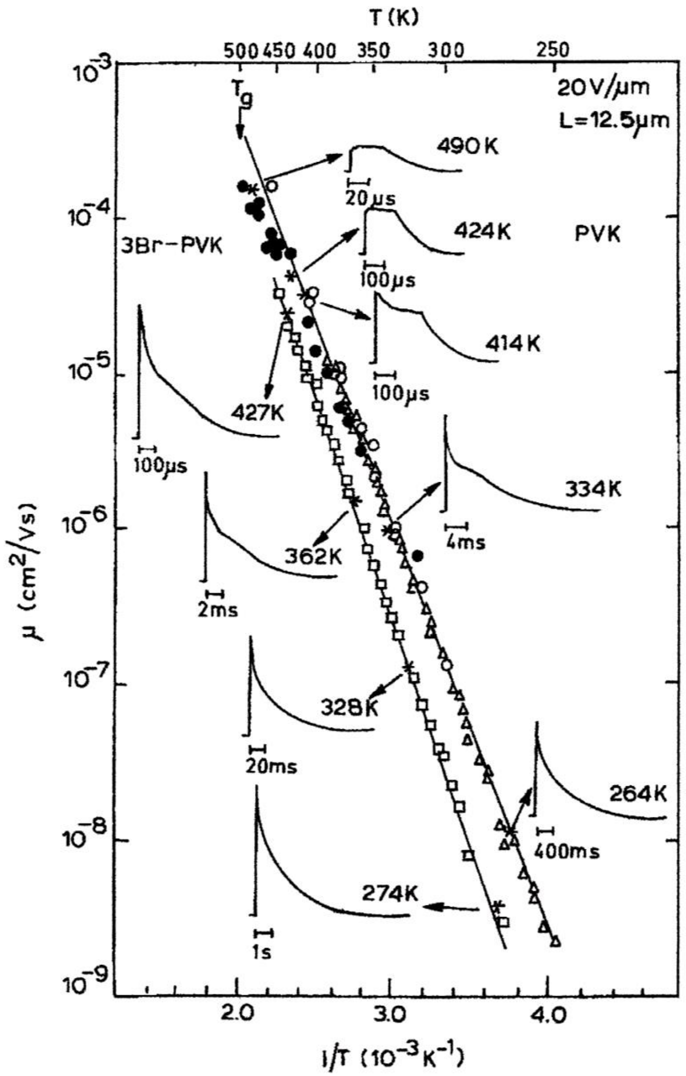
Physical Significance of α – Dispersive to Normal Transport Transition

- Transition occurs at α = 1
- Dispersive to normal transport transition occurs at when T = T_c
- T_c is temperature at which states are "frozen in"

$$\alpha(T) = \frac{kT}{E_c} = \frac{T}{T_c} \qquad \underset{\rightarrow}{\alpha = 1} \qquad T_{Transition} = T_c$$



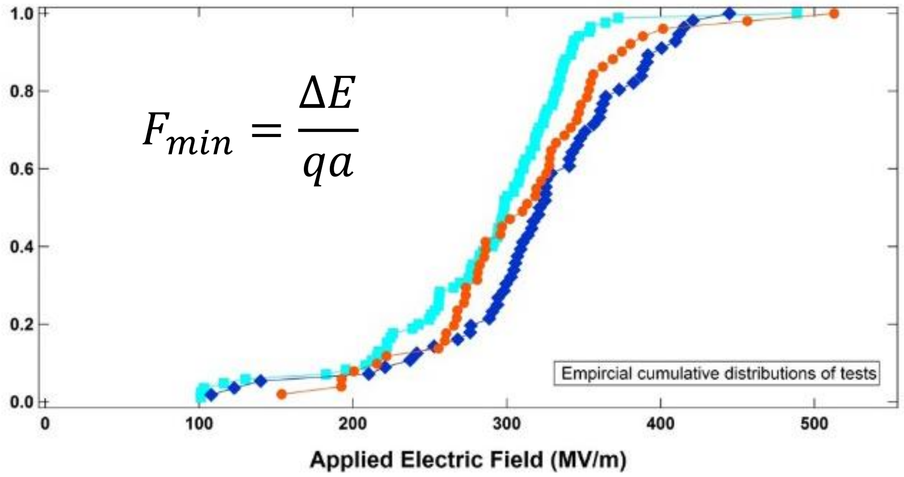
Temperature dependence of hole transport PVK and 3Br–PVK. Representative current traces are shown (after Pfister and Griffiths 1978).

(Pfister, 1978)

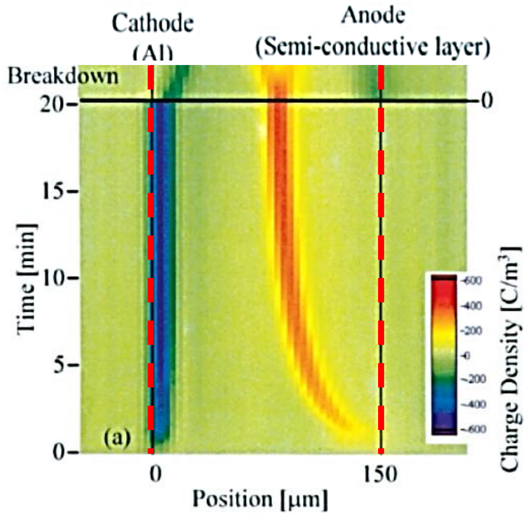
Physical Significance of α – Dispersive to Normal Transport Transition

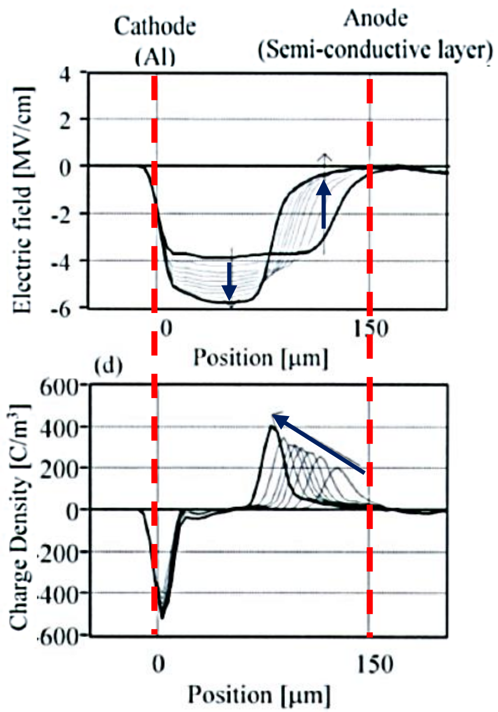
- Transition occurs at α = 1
- Dispersive to normal transport transition occurs at when $E = E_{Transition}$
- $E_{transition}$ denotes onset of electrostatic breakdown

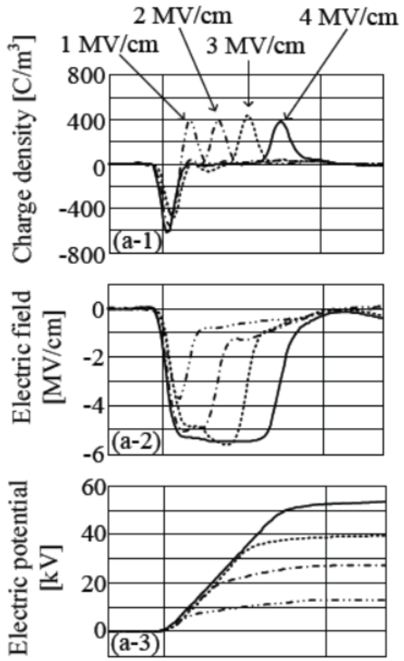
$$\alpha(E) = \frac{qaE}{2kT_c} \quad \xrightarrow{\alpha = 1} \quad E_{Transition} = \frac{2kT_c}{qa}$$



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





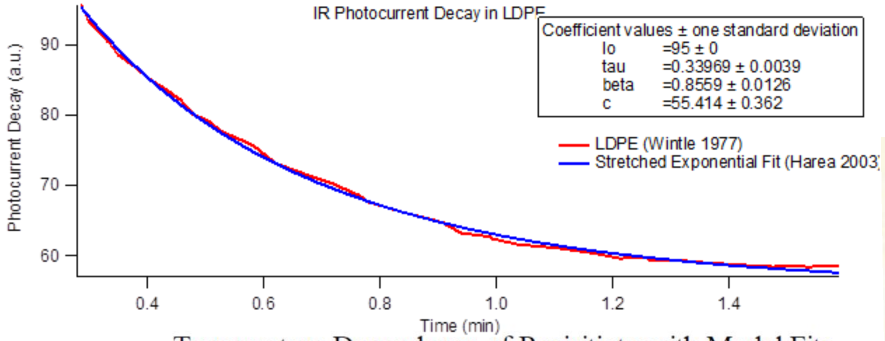


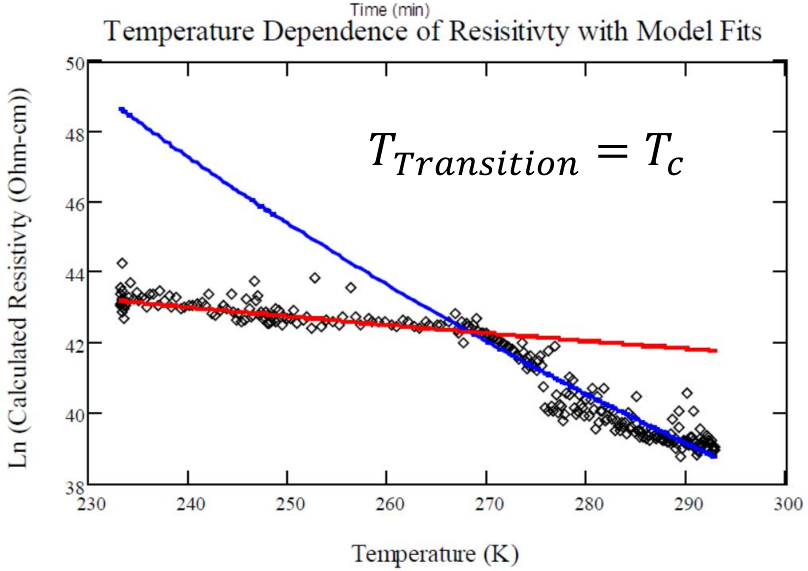
(Andersen, 2017; Matsui, 2005)

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

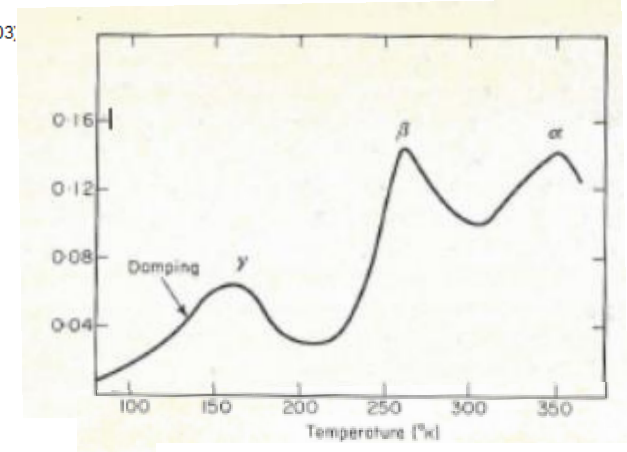
LDPE as an example

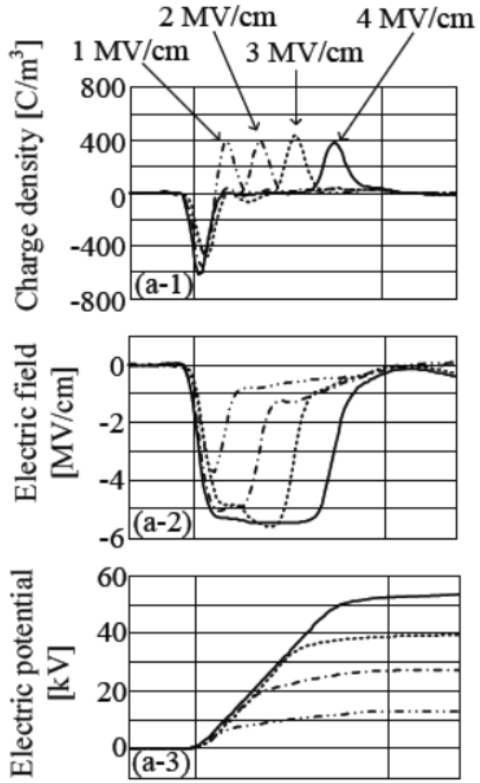
- T_c = 268 K from $\sigma(T)$
- β-phase transition at ~T_c
- ESD onset and dispersive to normal transport transition at E~100 MV/m
- RIC measurements predict T_c~255 K

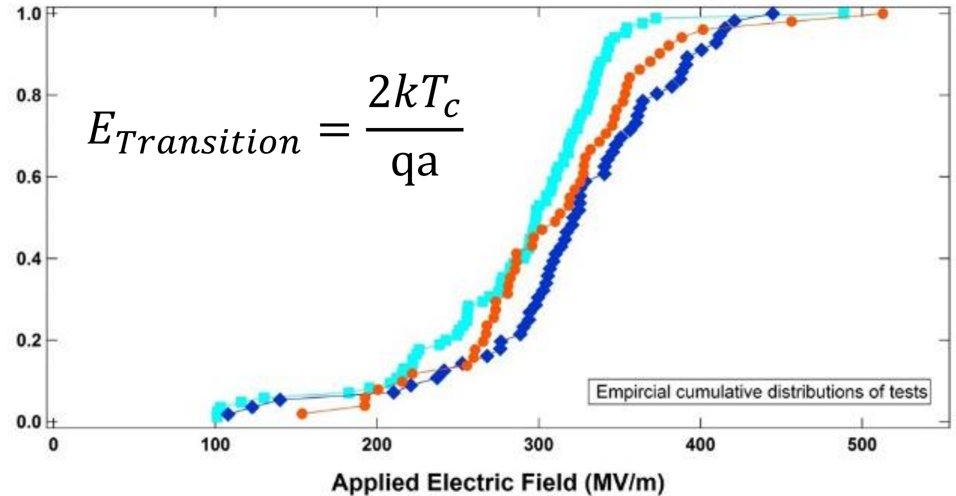




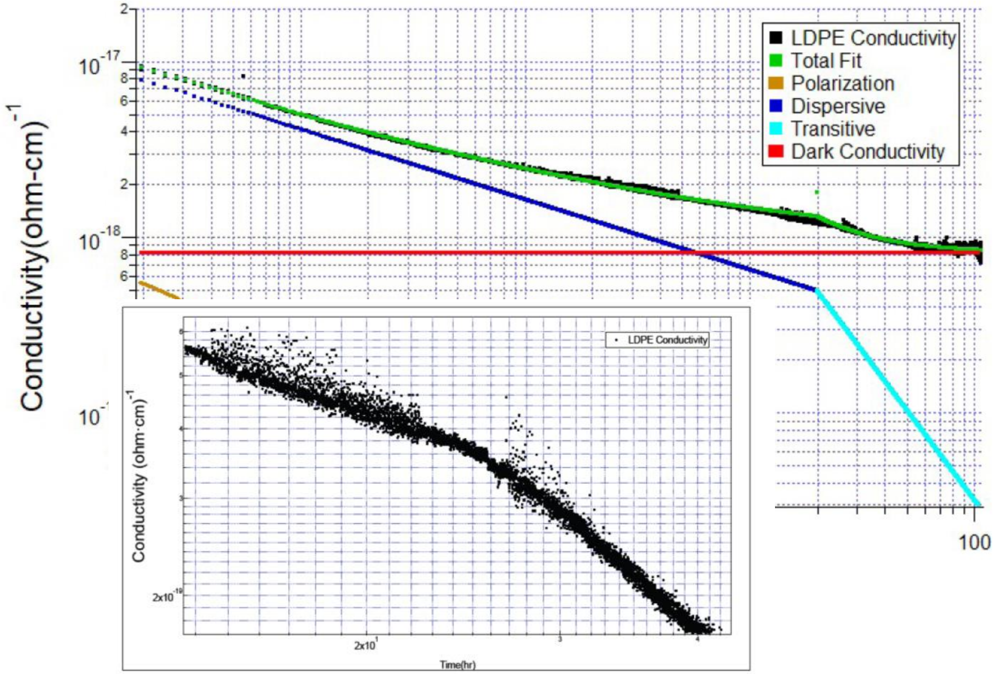
$$T_{Transition} = T_c$$







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



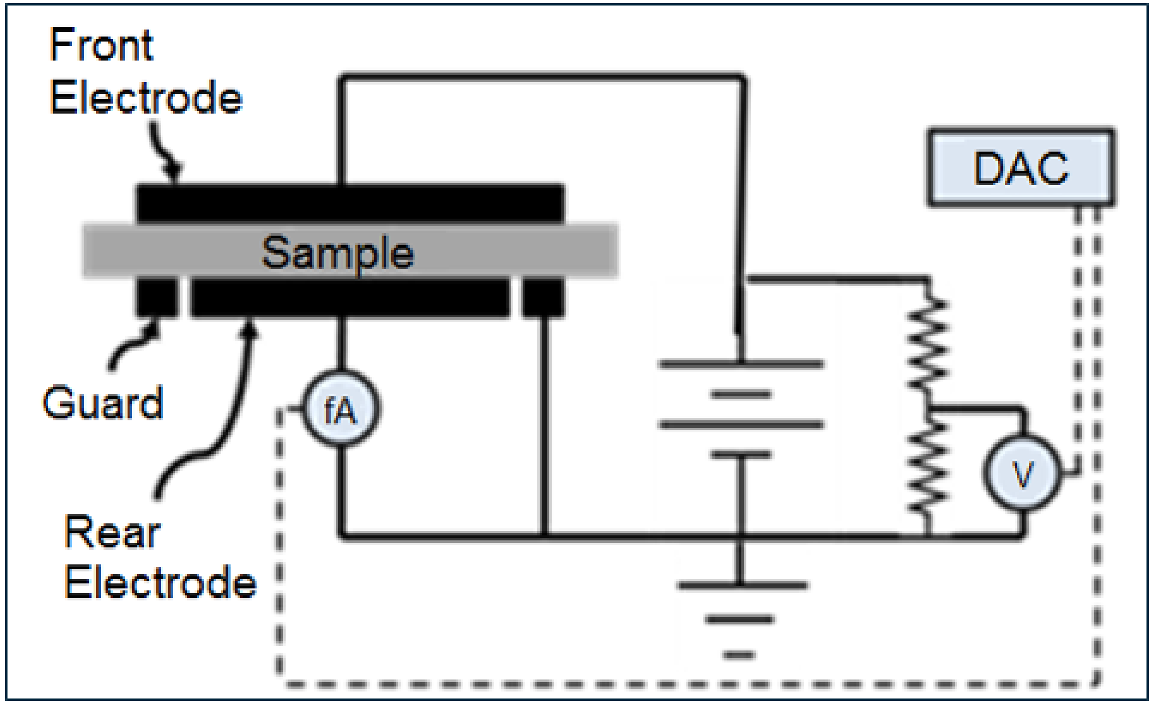
Conclusions

- 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

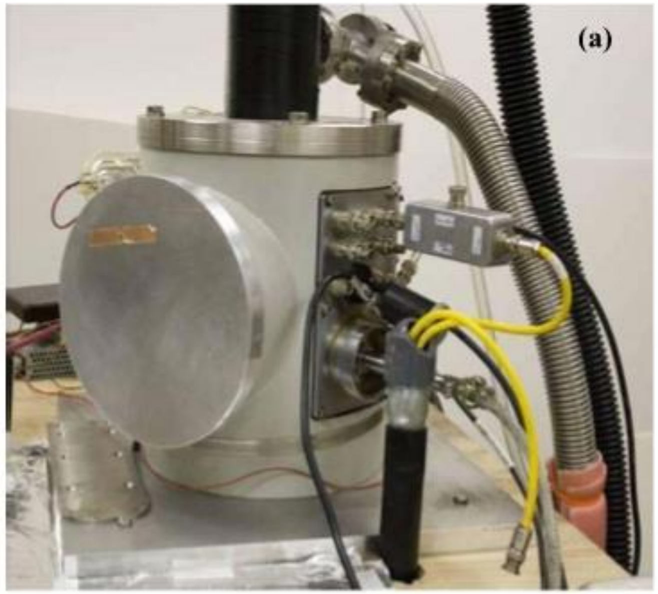
Future Work

- 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
  - In Progress

Constant Voltage Conductivity Chamber



Measurement limit of ~0.2 fA at ~900 V with 2 cm^2 area and 25 µm thick sample



Ohm's Law

$$V = I(\rho \frac{L}{A})$$

Resistance ($\rho \frac{L}{A}$)

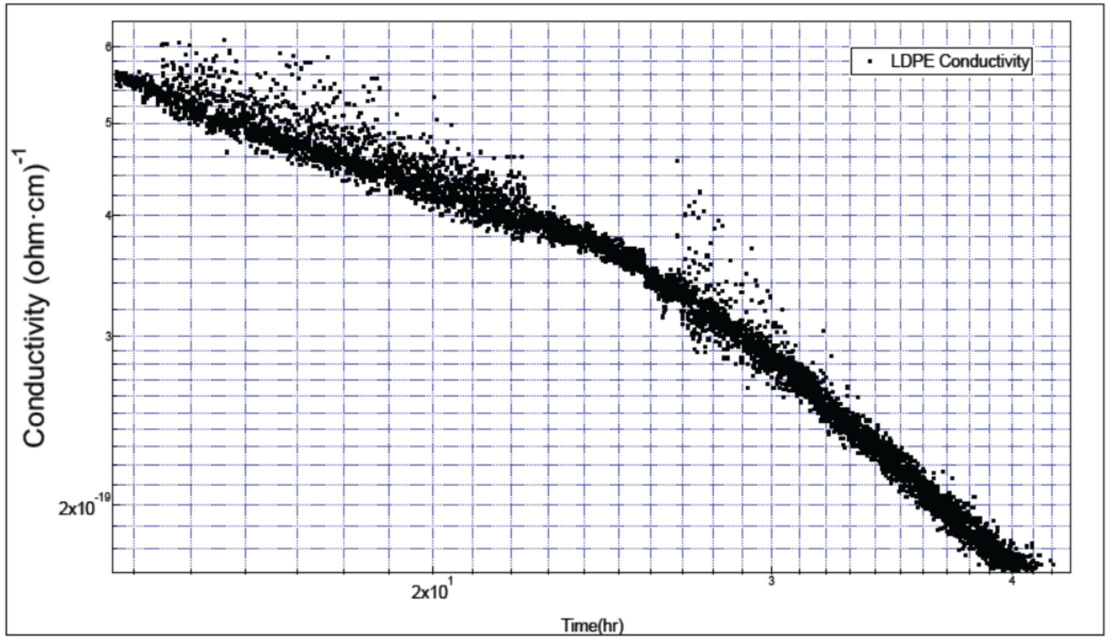
$$\rho(t) = \frac{V(t) * A}{I(t) * L}$$

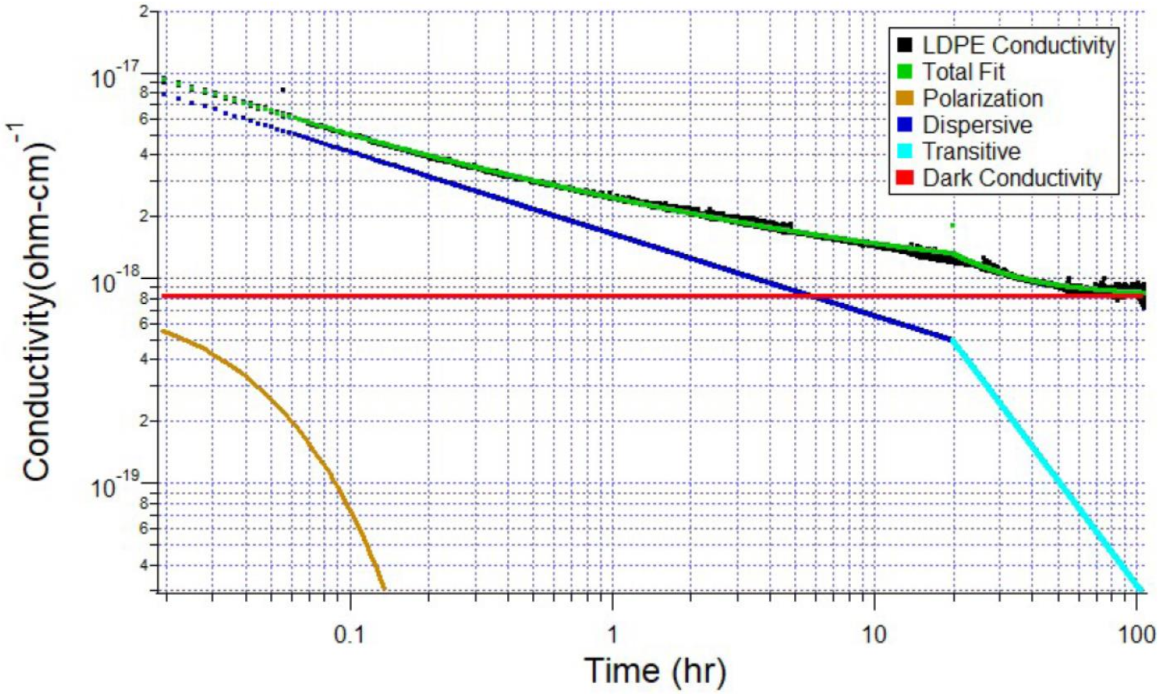
Voltage ($V(t)$), *Sample Area* (A), *Current* ($I(t)$), *Sample Thickness* (L)

$$\sigma = \frac{1}{\rho}$$

DC Conductivity

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

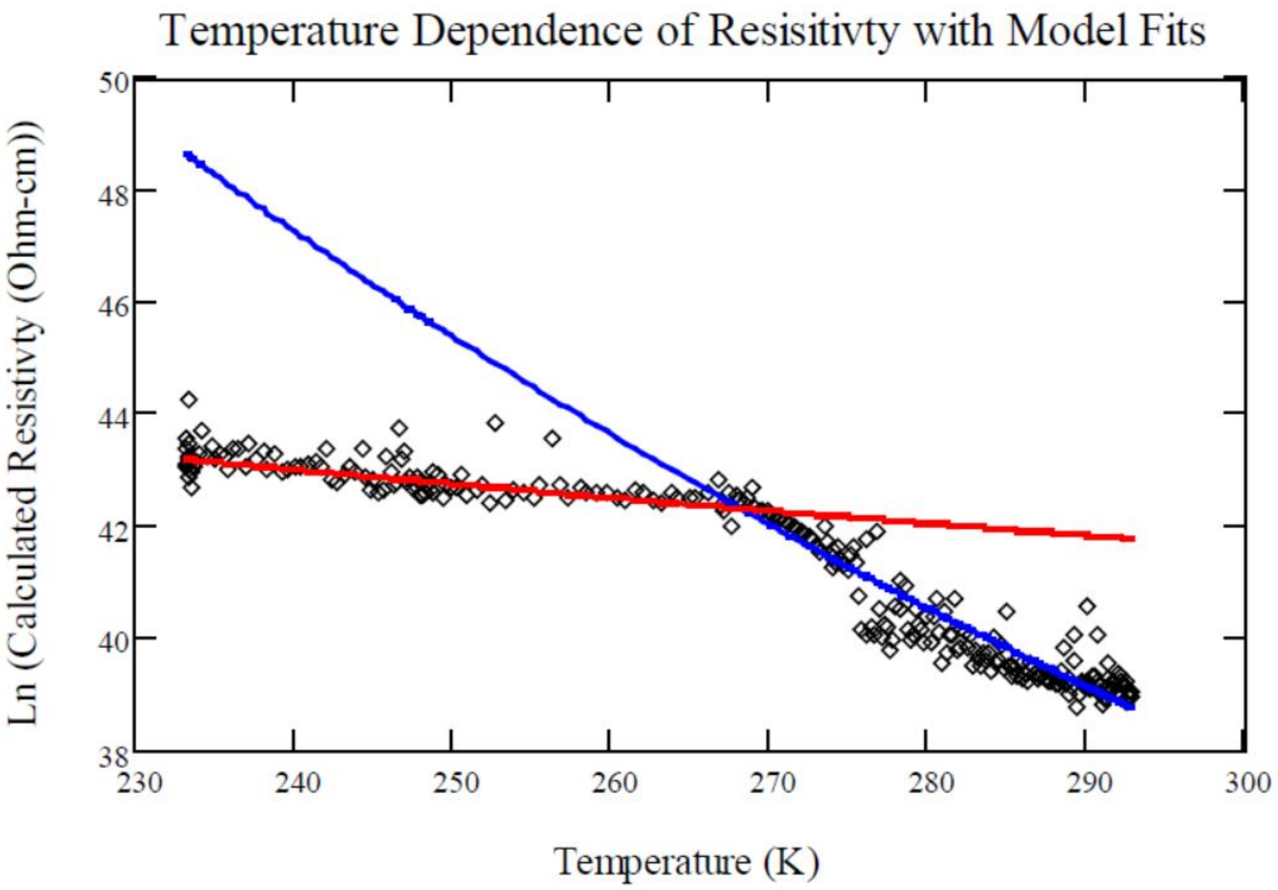




$$\sigma(t) = \sigma_P{}^{\frac{-t}{\tau_P}} + \{\sigma_{disp} t^{-(1-\alpha)} \theta(\tau_{transit} - t) + \sigma_{trans} t^{-(1+\alpha)} \theta(t - \tau_{transit})\} + \sigma_{DC}$$

(Wood, 2018)

Previous Resistivity Tests

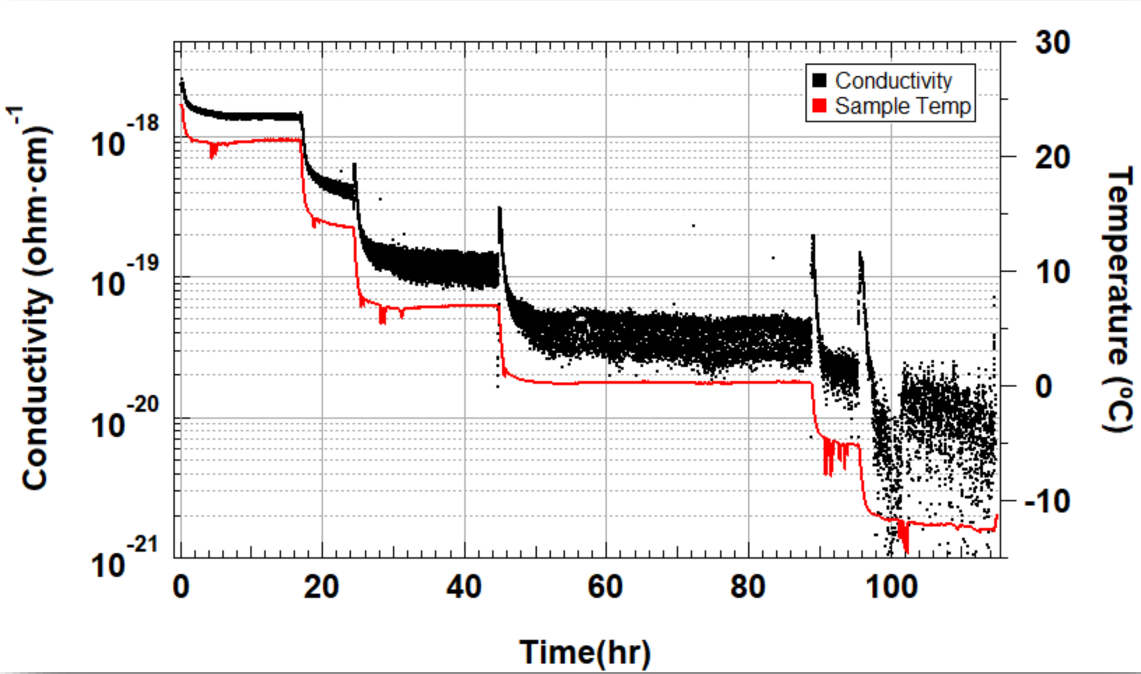


- Data to the left shows the change in resistivity with temperature previously taken with the CVC chamber
- The change in resistivity occurs around 270 K
  - transition from multiple trapping to variable range hopping
- Current tests are shown as conductivity instead of resistivity having a relationship of

$$\sigma = \frac{1}{\rho}$$

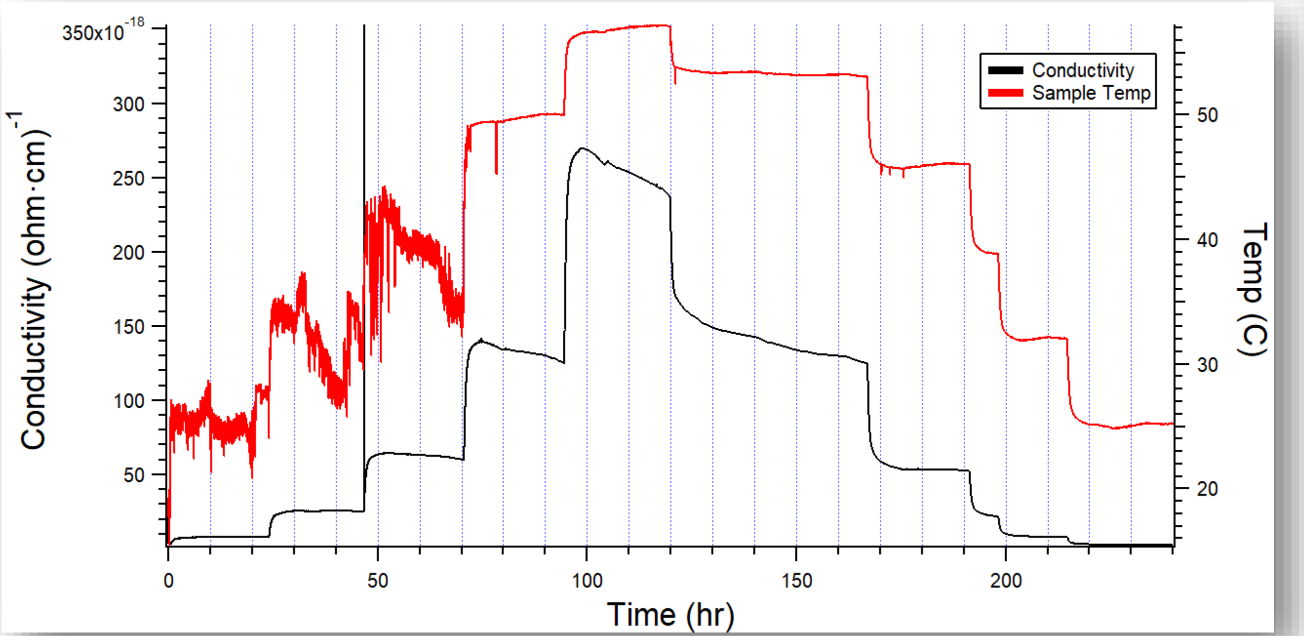
(Dennison, 2008; Brunson, 2007)

CVC Temperature Runs



Hot Temperature Run

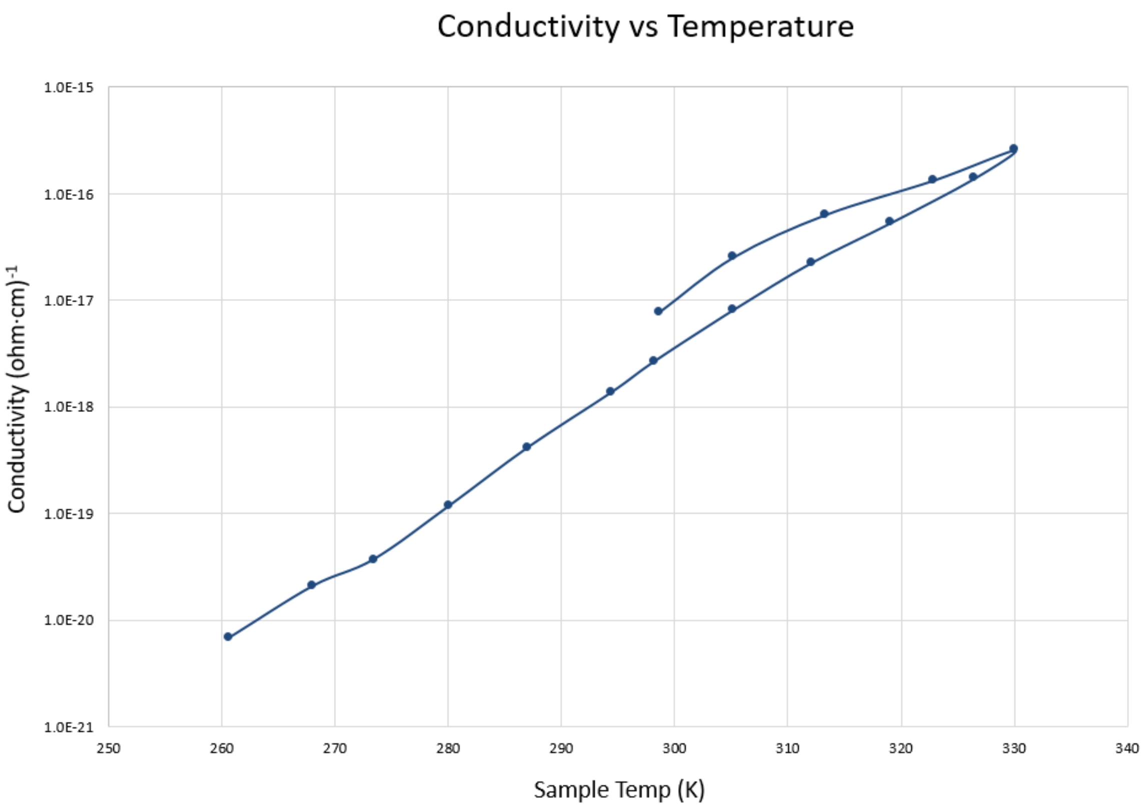
- Temperature steps of ~8 ^oC were taken from room temperature to ~57 ^oC and then back down
- Each step was allowed to come close to an equilibrium over several hours

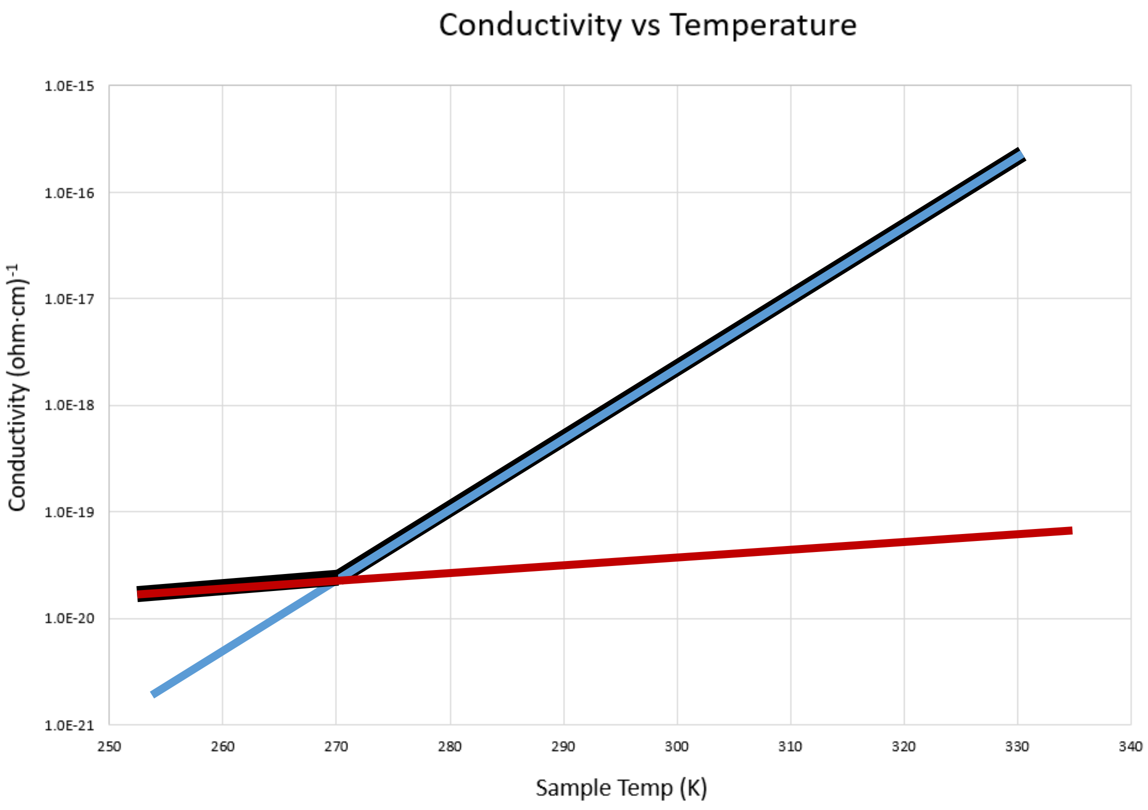


Cold Temperature Run

- Temperature steps again of ~8 ^oC were taken from room temperature down to ~-12 ^oC
- 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

1. Zallen, R. (1983). The physics of amorphous solids: John Wiley and Sons.
2. Sim, A. (2013). *Unified model of charge transport in insulating polymeric materials.* (PhD), Utah State University.
3. Scher, H., & Montroll, E. W. (1975). Anomalous transit-time dispersion in amorphous solids. *Physical Review B, 12*(6), 2455.
4. Pfister, G., & Scher, H. (1978). Dispersive (non-Gaussian) transient transport in disordered solids. *Advances in Physics, 27*(5), 747-798.
5. Cole, K. S., & Cole, R. H. (1941). Dispersion and absorption in dielectrics I. Alternating current characteristics. *The Journal of Chemical Physics, 9*(4), 341-351.
6. Cole, K. S., & Cole, R. H. (1942). Dispersion and absorption in dielectrics II. Direct current characteristics. *The Journal of Chemical Physics, 10*(2), 98-105.
7. Wood, B., King, D., & Dennison, J. (2018). Time-Evolved Constant Voltage Conductivity Measurements of Common Spaceborne Polymeric Materials. *IEEE Transactions on Plasma Science*.
8. Wintle, H. (1977). Photoelctric Effects in Insulating Polymers and Their Relation to Conduction Processes. *IEEE Transactions on Electrical Insulation*(2), 97-113.
9. Harea, D., Vasilev, I., Colomeico, E., & Iovu, M. (2003). Persistent photoconductivity in amorphous As2Se3 films with Sn impurity. *J Optoelectron Adv Mater, 5*(5), 1115.
10. Brunson, J., & Dennison, J. (2007). LOW TEMPERATURE MEASUREMENTS OF RESISTIVITY IN LOW-DENSITY POLYETHYLENE.
11. Dennison, J., & Brunson, J. (2008). Temperature and electric field dependence of conduction in low-density polyethylene. *IEEE Transactions on Plasma Science, 36*(5), 2246-2252.
12. Gillespie, J. (2013). *Measurements of the Temperature Dependence of Radiation Induced Conductivity in Polymeric Dielectrics.* (MS), Utah State University.
13. Tyutnev, A., Saenko, V., Smirnov, I., & Pozhidaev, E. (2006). Radiation-induced conductivity in polymers during long-term irradiation. *High Energy Chemistry, 40*(5), 319-330.
14. Metzler, R., & Klafter, J. (2004). The restaurant at the end of the random walk: recent developments in the description of anomalous transport by fractional dynamics. *Journal of Physics A: Mathematical and General, 37*(31), R161.
15. Schmidlin, F. W. (1977). Theory of trap-controlled transient photoconduction. *Physical Review B, 16*(6), 2362.
16. Adhikari, P., Kobbekaduwa, K., Shi, Y., Zhang, J., Al Abass, N., He, J., . . . Gao, J. (2018). Sub-50 picosecond to microsecond carrier transport dynamics in pentacene thin films. *Applied Physics Letters, 113*(18), 183509.
17. Tiedje, T., & Rose, A. (1981). A physical interpretation of dispersive transport in disordered semiconductors. *Solid State Communications, 37*(1), 49-52.
18. Matsui, K., Tanaka, Y., Takada, T., Fukao, T., Fukunaga, K., Maeno, T., & Alison, J. M. (2005). Space charge behavior in low density polyethylene at pre-breakdown. *IEEE transactions on dielectrics and electrical insulation, 12*(3), 406-415.
19. Andersen, A., Dennison, J., & Moser, K. (2017). Perspectives on the Distributions of ESD Breakdowns for Spacecraft Charging Applications. *IEEE Transactions on Plasma Science, 45*(8), 2031-2035.
20. McCrum, E., Read, B. E., & Williams, G. (1967). Hydrocarbon Polymers *Anelastic and Dielectric Effects in Polymeric Solids* (pp. 353). London: John Wiley and Sons.