Charge transport in Organic Semiconductors: Role of disorder, correlation and morphology

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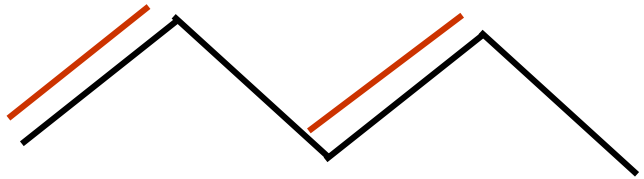
Based on the collaborative work with Dr. S. Rajmohan and Dr. M. P. Joshi

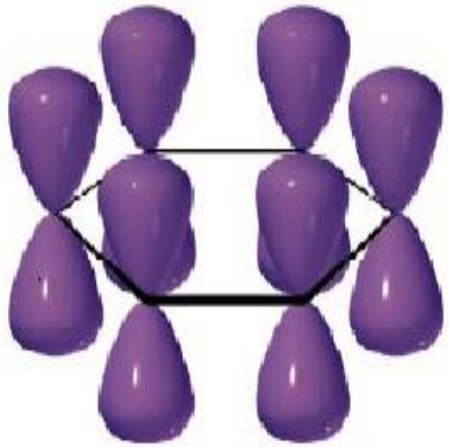
Organic Semiconductors

- **Basically carbon compounds with conjugated bonds in their structure (Alternate double and single bond).**

C – C = C – C



- **The weak π-bond establishes a *delocalized electron density* above and below the plane of the carbon atoms.**

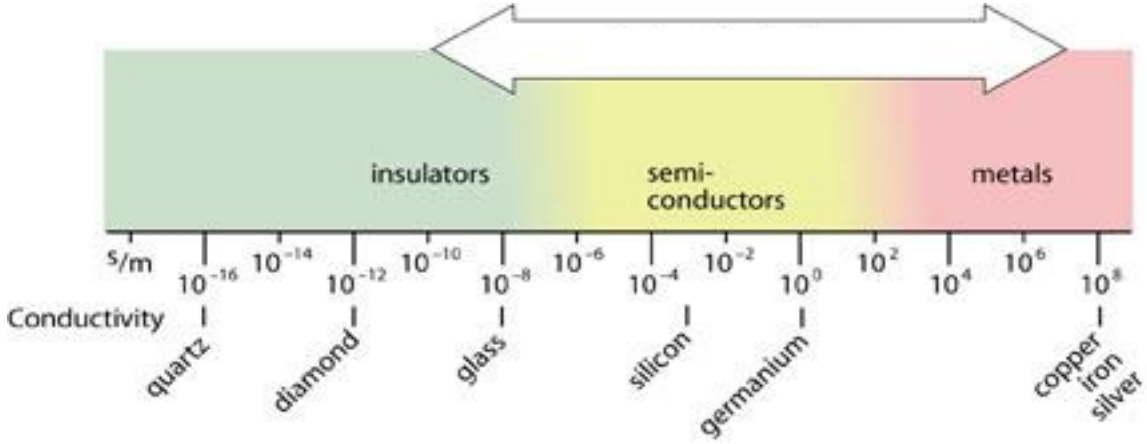


Ref: Pope and C. E. Swenberg, Electronic Processes in Organic Crystals and Polymers, 2nd Edition (Oxford University Press, New York, 1999).

❖ **HOMO-LUMO gap is the range of 1eV - 3.5eV**

❖ **Some materials do show high luminescence**

❖ **Doping is possible (Conductivity tuning)**

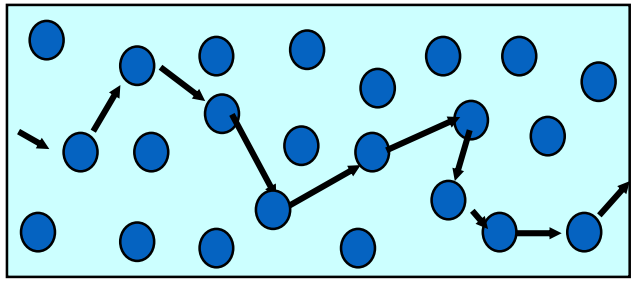


❖ **Mobility is in the range of $1x10^{-7}$~$1x10^{-3}$ cm^2/Vs**

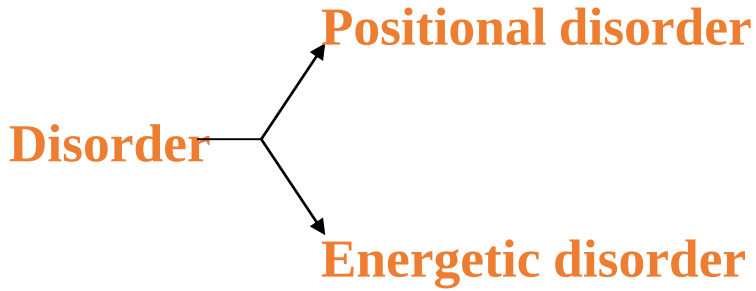
Charge Transport in Disorder Thin Films

- **Charge transport occurs by means of hopping**
  - ❖ **Weak inter molecular interaction (Vander-walls force) :: *Localized states***
- **Gaussian Disorder Model :: *(Widely used for analyzing charge transport)***

  Ref:: Bassler, Phys. stat. solidi. (b) 175, 15, 1993.



$\overrightarrow{E}$

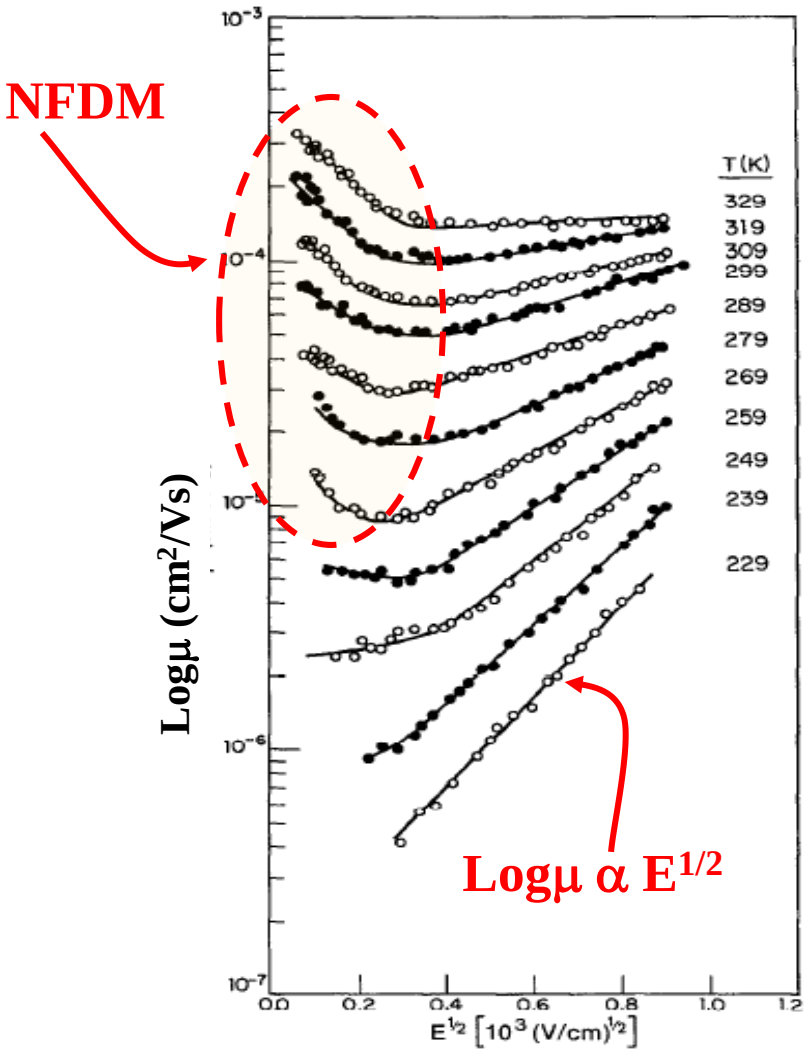


- **Site energies are assumed to follow Gaussian distribution**

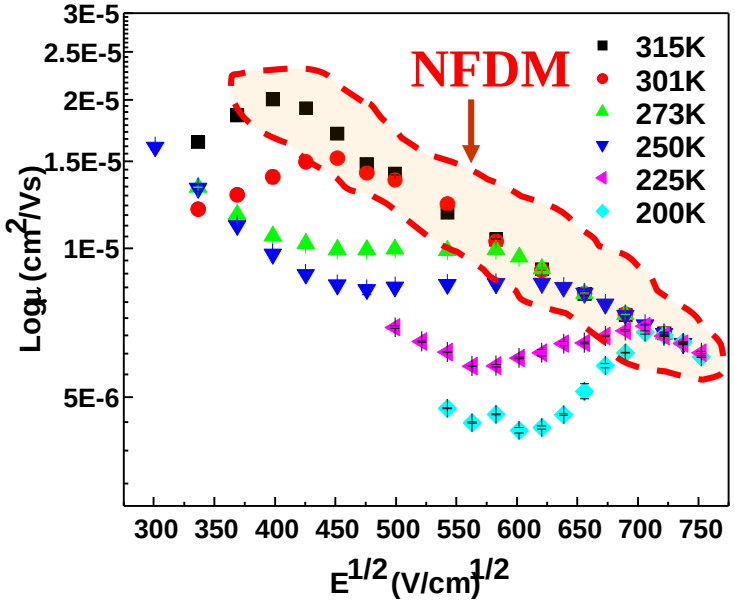
$\rho(\varepsilon) = (2\pi\sigma^2)^{-1/2}\exp(-\varepsilon^2/2\sigma^2)$

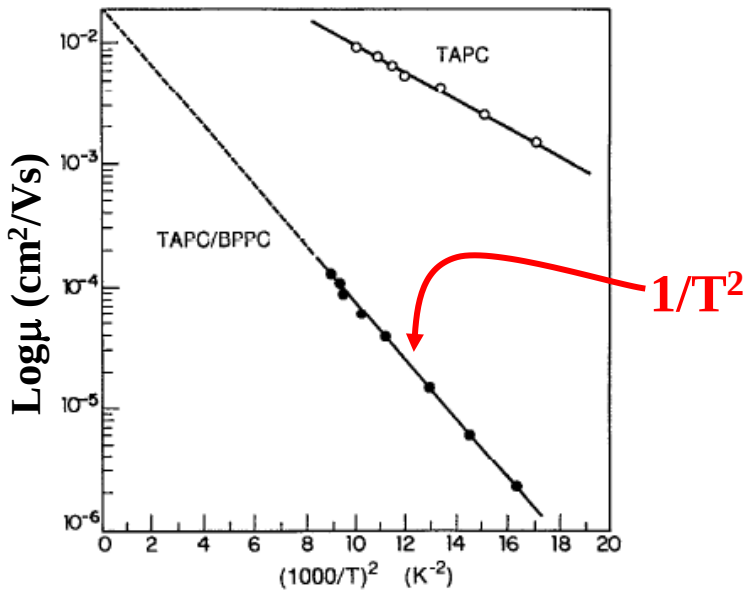
$$\mu = \mu_o \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right]\exp\left[C\left\{\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right\}E^{\frac{1}{2}}\right]$$

Typical Charge Transport behavior



J. Chem. Phys., 94 (1993) 5449

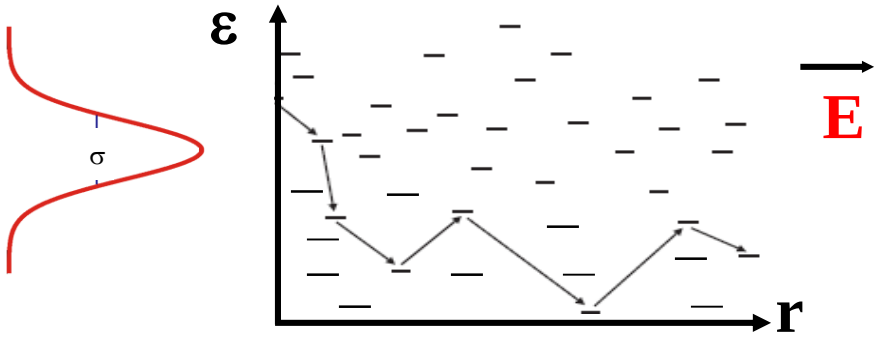


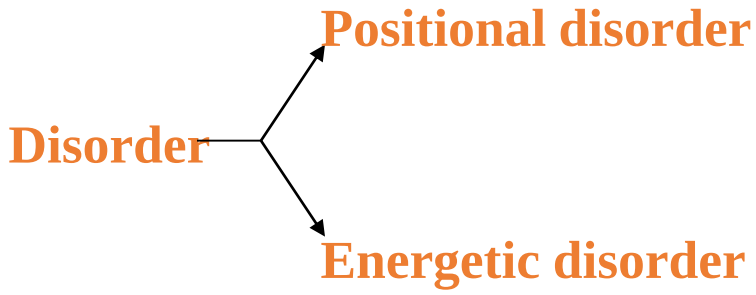


Negative field dependence of mobility (NFDM)

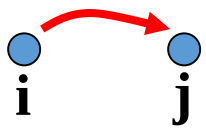
Gaussian Disorder Model (GDM)

Bassler, Phys. Stat. Solidi. (b) 175, 15, 1993.





- Gaussian Density of states : $\rho(\varepsilon) = (2\pi\sigma^2)^{-1/2}\exp(-\varepsilon^2/2\sigma^2)$
- Gaussian distribution : wave function overlap parameters
- Jump rate is governed by Miller - Abrahams equation

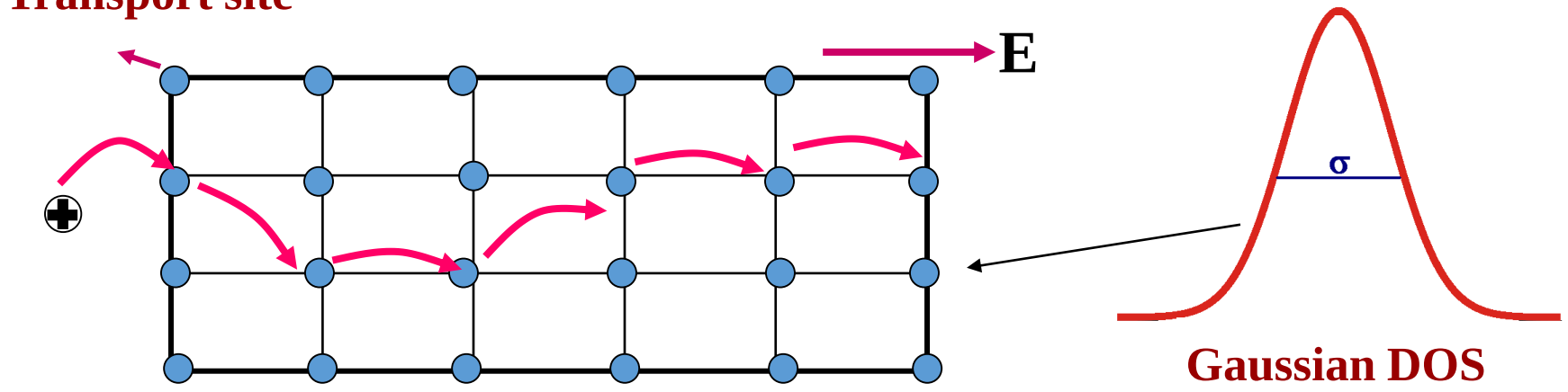


$$\nu_{ij} = \nu_0 \exp\left(-2\gamma a \frac{\Delta R_{ij}}{a}\right) \begin{cases} \exp\left(-\frac{\varepsilon_i - \varepsilon_j}{kT}\right)\exp\left(\pm\frac{eEa}{kT}\right) & , \quad \varepsilon_j > \varepsilon_i \\ 1 & , \quad \varepsilon_j < \varepsilon_i \end{cases}$$

- Drift mechanism of charge transport for the entire field range. ($\mu = L / E\tau$)

Monte Carlo Simulations

Bassler, Phys. Stat. Solidi. (b) 175, 15, 1993.



- Through out the simulation we assume zero positional disorder, Σ= 0
- Jump rates are governed by Miller- Abraham equation,

$$\nu_{ij} = \nu_0 \exp\left(-2\gamma a \frac{\Delta R_{ij}}{a}\right) \begin{cases} \exp\left(-\frac{\varepsilon_i - \varepsilon_j}{kT}\right)\exp\left(\pm\frac{eEa}{kT}\right) & , \quad \varepsilon_j > \varepsilon_i \\ 1 & , \quad \varepsilon_j < \varepsilon_i \end{cases}$$

- Average carrier transit time (τ) for a sample length 4μm was calculated by averaging over few hundred carriers. $\mu = L^2 / V\tau$ (cm^2/ Vs)

Monte Carlo simulations

(G. Schönherr, H. Bässler, M. Silver, Philos. Magz., 44, 47, 1981)

- **Lattice of 70x70x300 (array) was generated along x, y and z direction.**
  - **Field was applied along z direction and intersite distance ~ 6Å.**
  - **Site energies: Assigned randomly from a Gaussian distribution**

$$\rho(\varepsilon) = \left(2\pi\sigma^2\right)^{-1/2} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right)$$

  - **Boundary condition is applied along x, y and z direction**
  - **Simulation always performed for a sample length 4μm along z direction is realized.**
- **Positional disorder inside the lattice was assumed to be zero.**
- **Hopping rate between sites *i* and *j* is governed by Miller-Abrahams equation,**

$$\nu_{ij} = \nu_0 \exp\left(-2\gamma a \frac{\Delta R_{ij}}{a}\right) \begin{cases} \exp\left(-\frac{\varepsilon_i - \varepsilon_j}{kT}\right)\exp\left(\pm\frac{eEa}{kT}\right) & , \quad \varepsilon_j > \varepsilon_i \\ 1 & , \quad \varepsilon_j < \varepsilon_i \end{cases}$$

Monte Carlo Simulations

Bassler, Phys. Stat. Solidi. (b) 175, 15, 1993.

- **Carrier was started from the first plane and it jumps to a new site which was determined from the probability (P_{ij}) calculated for each 7x7x7 sites around the carrier.**

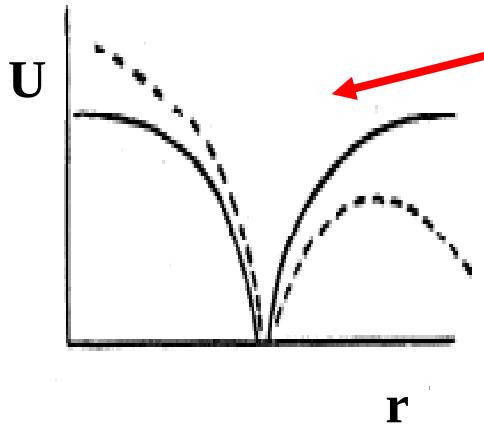
$$P_{ij} = \frac{\nu_{ij}}{\sum_{i \neq j} \nu_{ij}} \qquad t_{ij} = \frac{x_{ei}}{\sum_{i \neq j} \nu_{ij}}$$

- **Average carrier transit time (τ) was calculated by averaging over 150 carriers.**

- **Mobility was calculated using**

$$\mu = L^2 / V\tau \ \ (cm^2 / Vs)$$

GDM: *Explanation of Charge transport behavior*

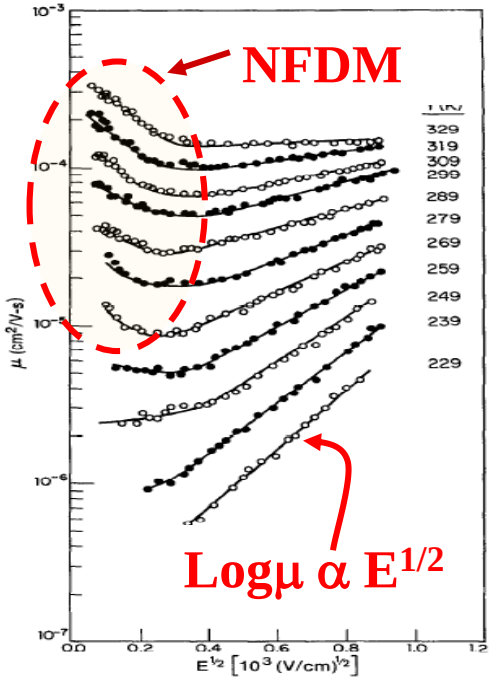


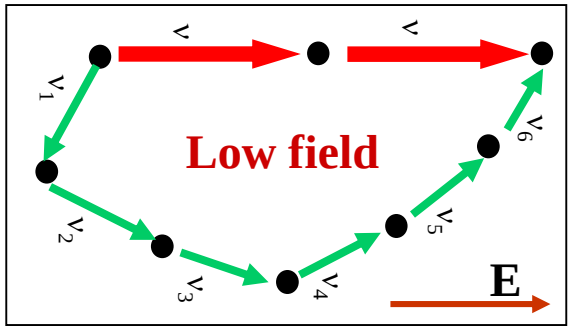
❖ *Logμ α $E^{1/2}$: Tilting of DOS by the applied field reduces the barrier seen by the carrier due to energetic disorder.*

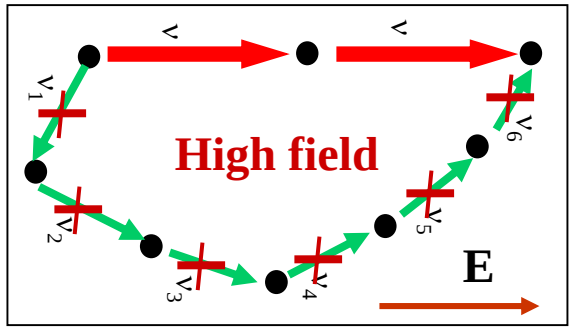
❖ **NFDM (i)** *at high field regime is due to saturation of carrier drift velocity and hence* μ ~ 1/E

(ii) *at intermediate field regime is expected at high temperature where the carrier can gains high thermal energy .*

(iii) *at low field regime the high positional disorder open up numerous faster roots, with varying resistance, which may involve carrier jumps against the field direction.*







These faster roots, with varying resistance, will gradually get eliminated with increase of electric field resulting NFDM.

Bassler, Phys. Stat. Solidi. (b) 175, 15, 1993.

Charge Transport in Disorder Thin Films

- **Improved charge transport :: Higher mobility**

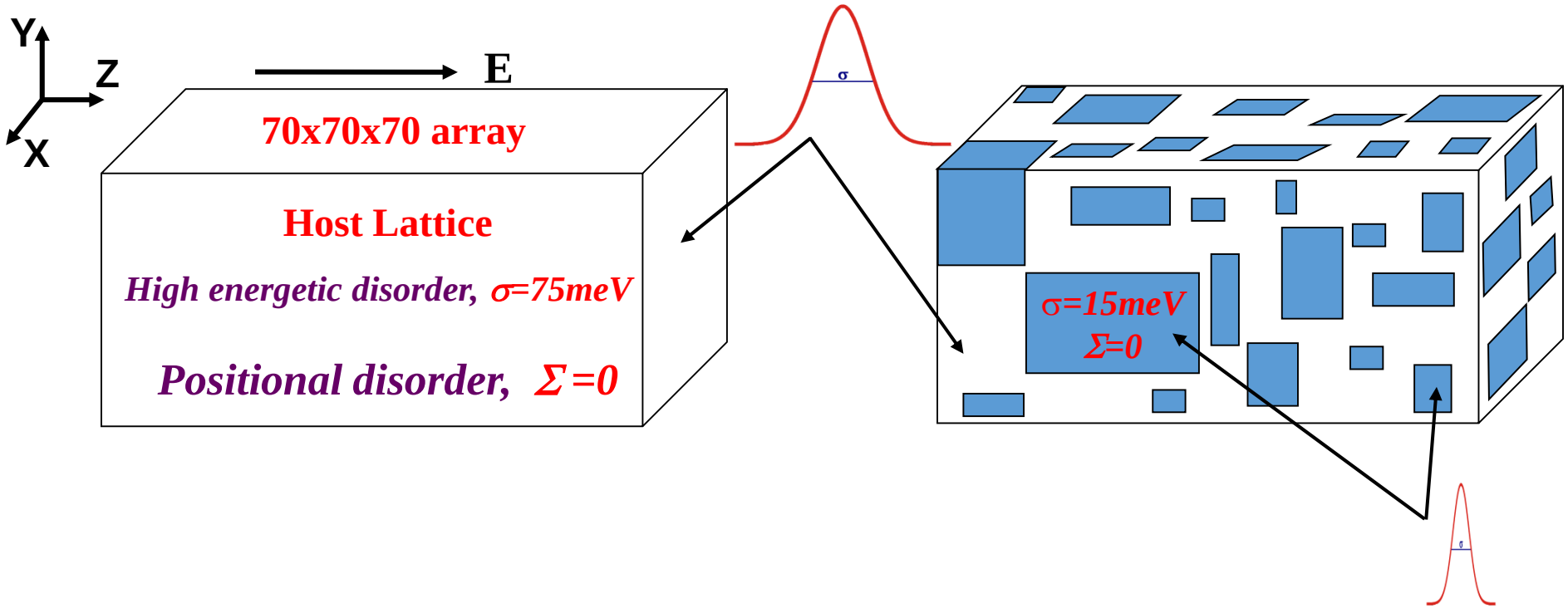
  - **Controlling the morphology of active organic layer**
    (controlling the processing condition)

    - **Annealing ::** ***Introducing ordered regions***

      (Understanding the influence of morphology on charge transport is highly important)

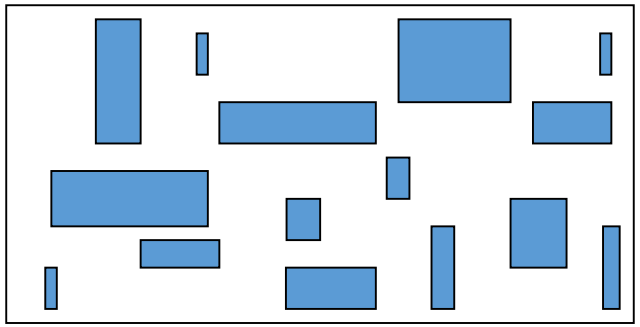
Simulating charge transport in a disordered lattice embedded with aggregates.

- ❖ Aggregates are ordered regions with low energetic disorder.
- ❖ Aggregates are embedded in a matrix of high energetic disorder.
- ❖ Size of aggregates vary randomly inside the matrix



Incorporating the effect of morphology on simulation

- **Morphology of the host lattice was modified by embedding cuboids of random sizes *(maximum size (*12x12x100*) nm)* placed randomly in a host lattice.**

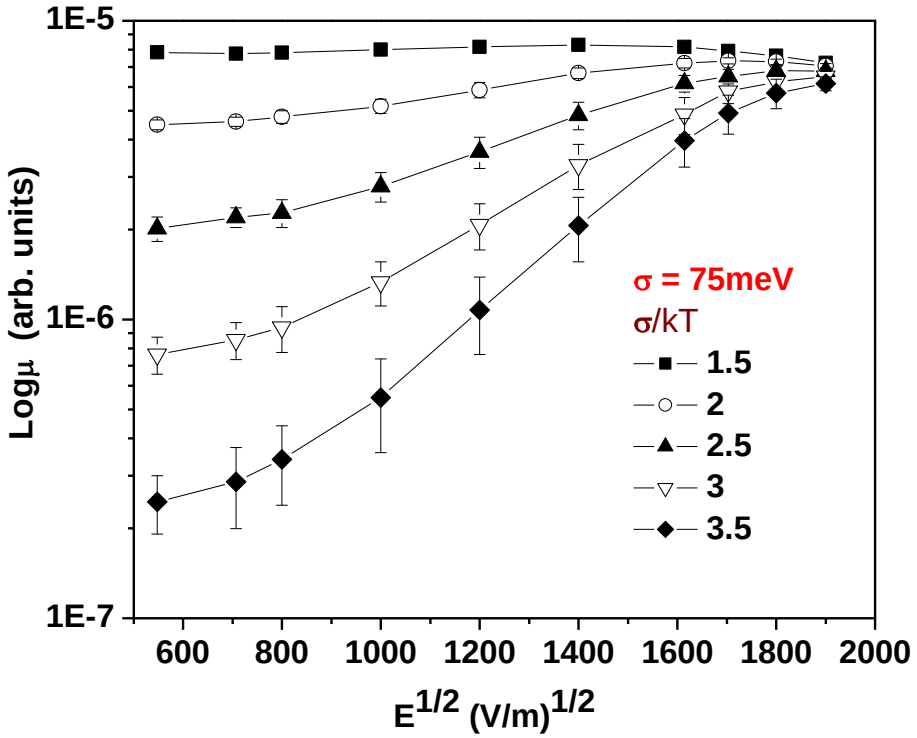


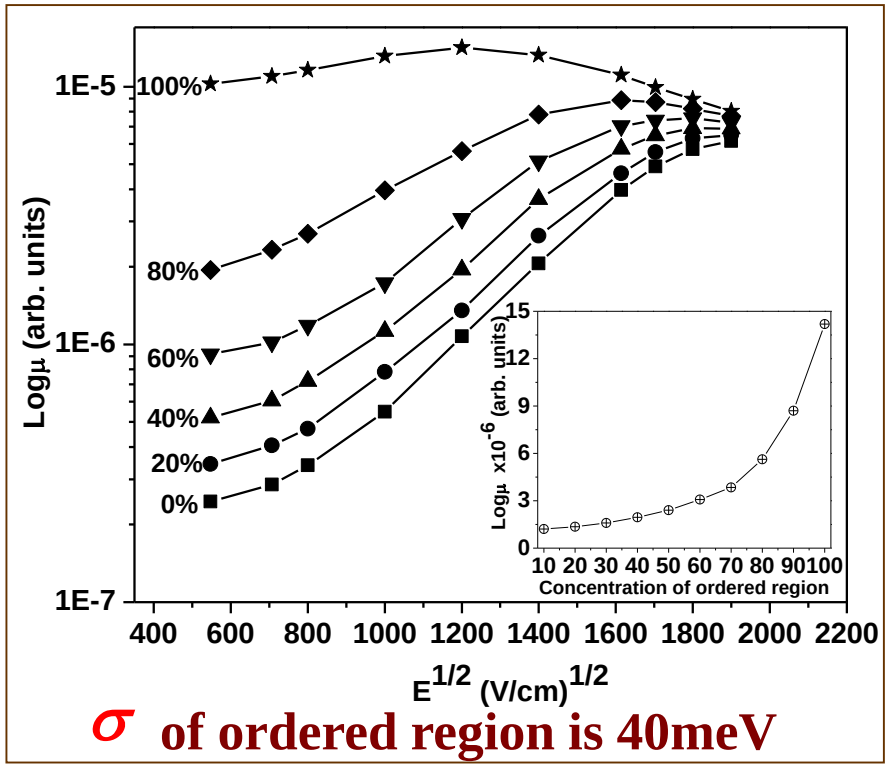
- **Positional disorder inside cuboids was also assumed to be zero.**

- **Influence of various parameters defining embedded cuboids, such as concentration of cuboids, energetic disorder, mean energy of DOS, on charge transport was investigated.**

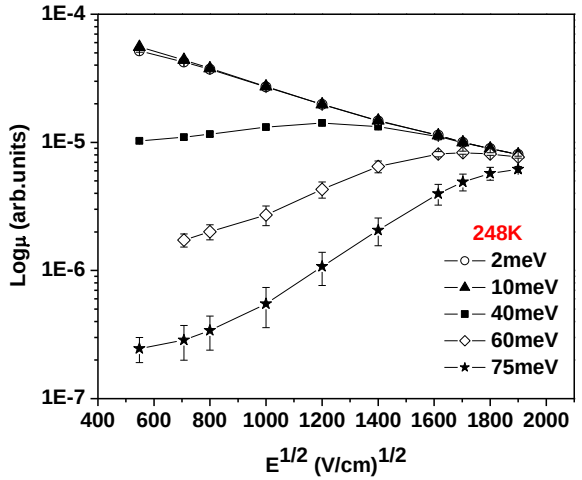
  - ***Energetic disorder of the host lattice was taken as 75meV. Host lattice is embedded with cuboids having energetic disorder either 60meV or 40meV or 2meV.***

Concentration of ordered regions inside host lattice





σ of ordered region is 40meV



- **Remarkable increase in mobility occur at 60% of ordered regions**

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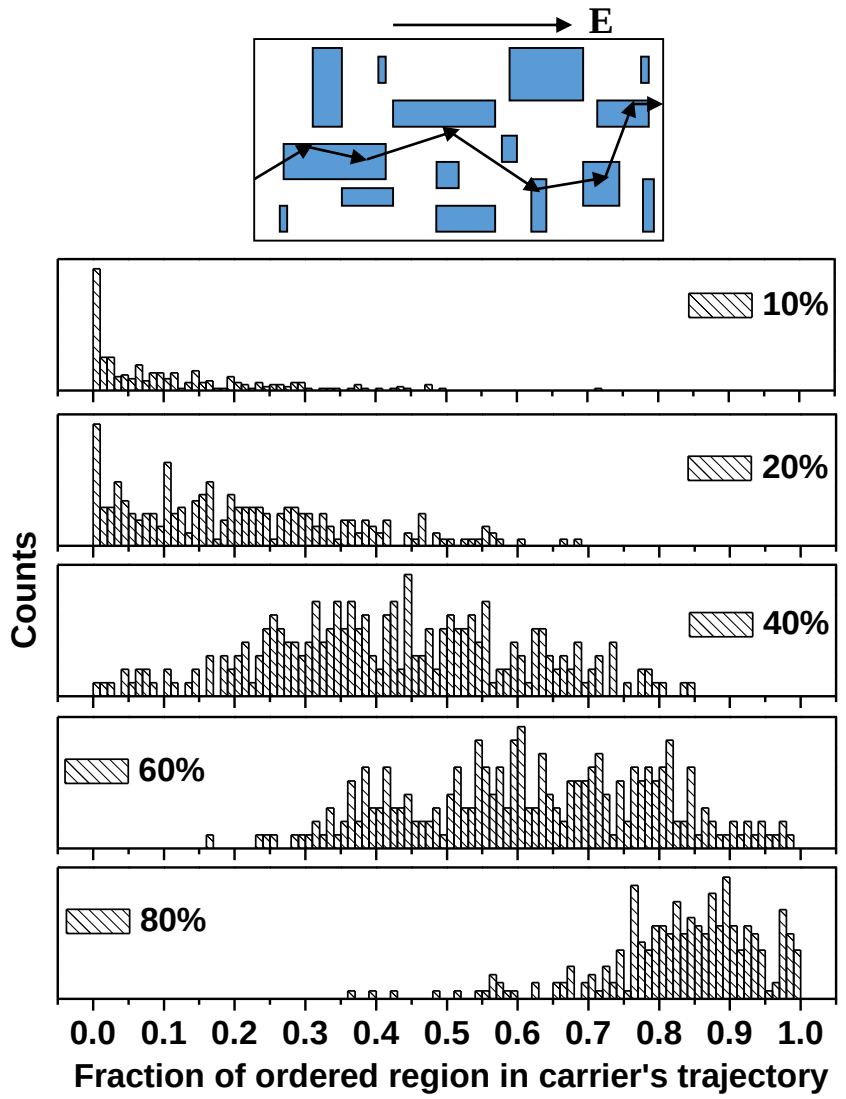
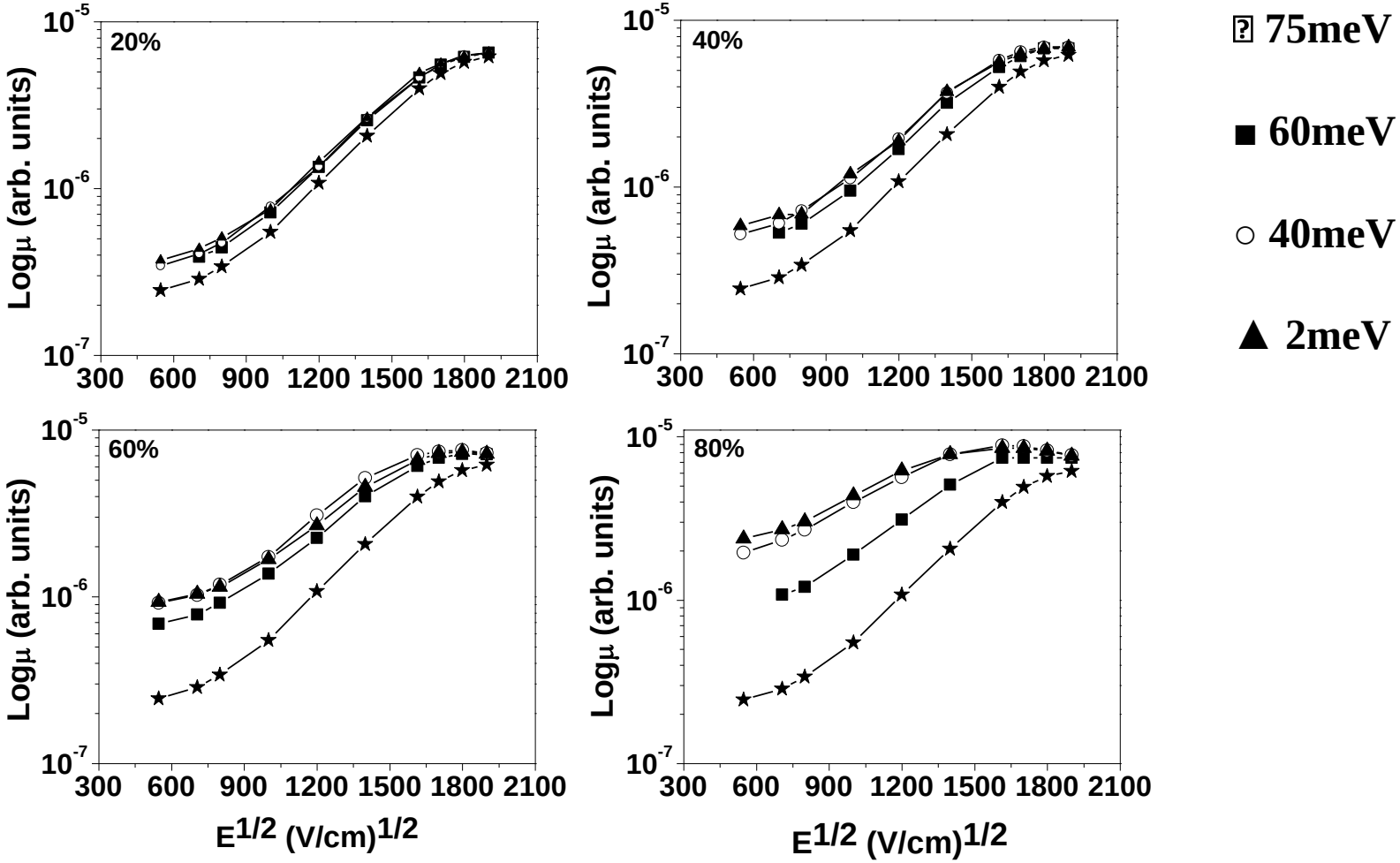
Path fraction of carriers

Organic Electronics 9 (2008) 355–368



Very few low resistant paths. High resistant paths are more.
Averaging over number of carriers results in low mobility.

Dependence of mobility on disorder inside the ordered regions



❖ **Remarkable influence of embedded ordered region was observed only at high concentrations**

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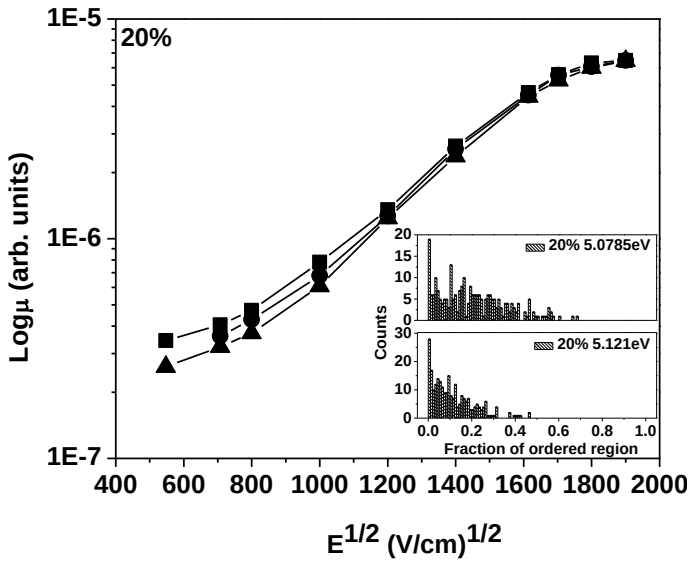
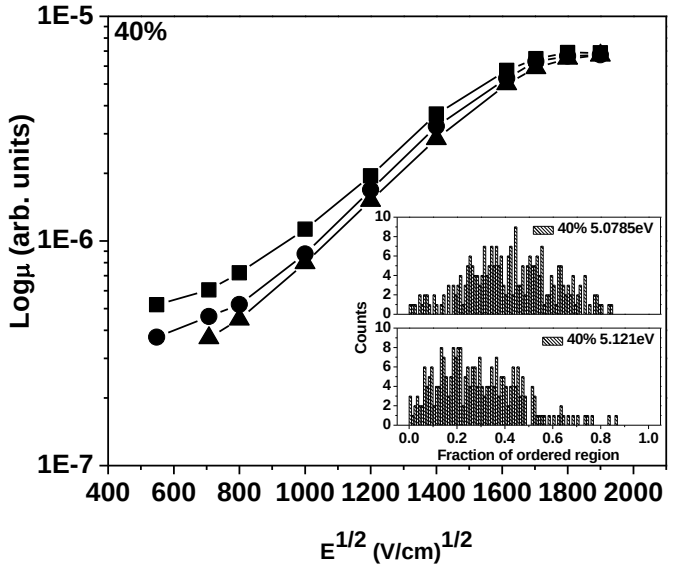
Influence of mean energy of DOS of ordered region

Mean energy of ordered region is taken such that difference with the mean energy of host lattice is in the order of kT





Level diagram

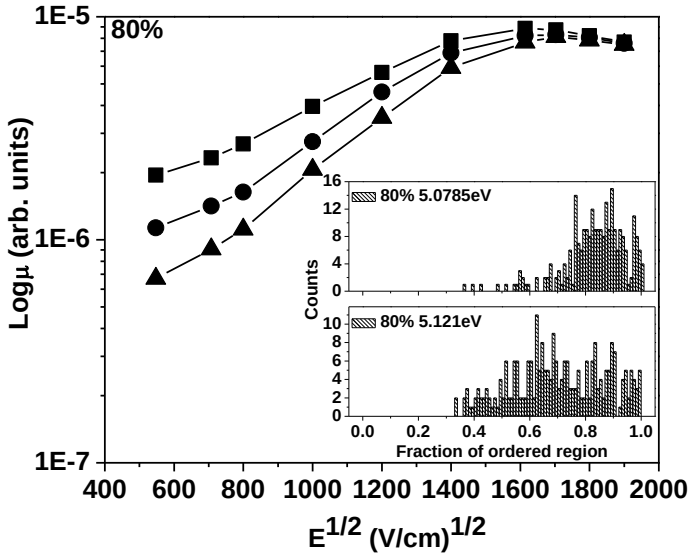
■ 5.0785 eV

5.10 eV ● 5.10 eV

Host

▲5.121 eV

Embedded region



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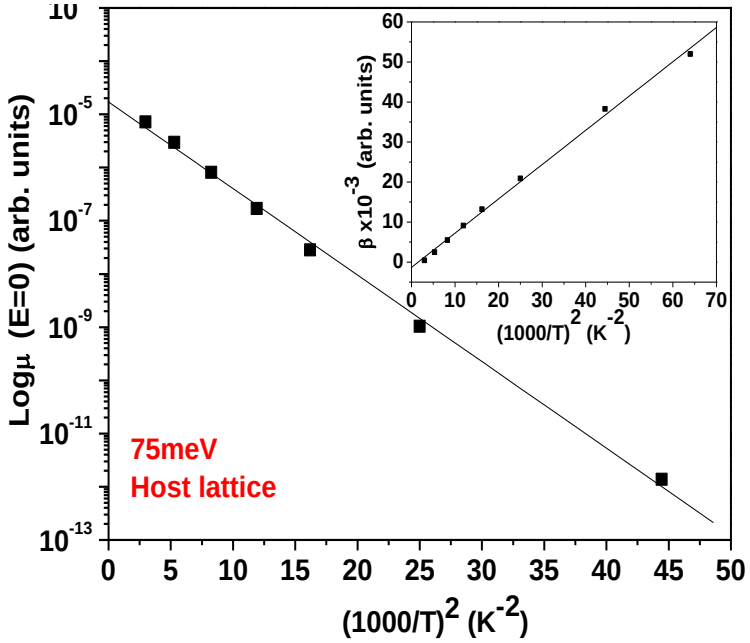
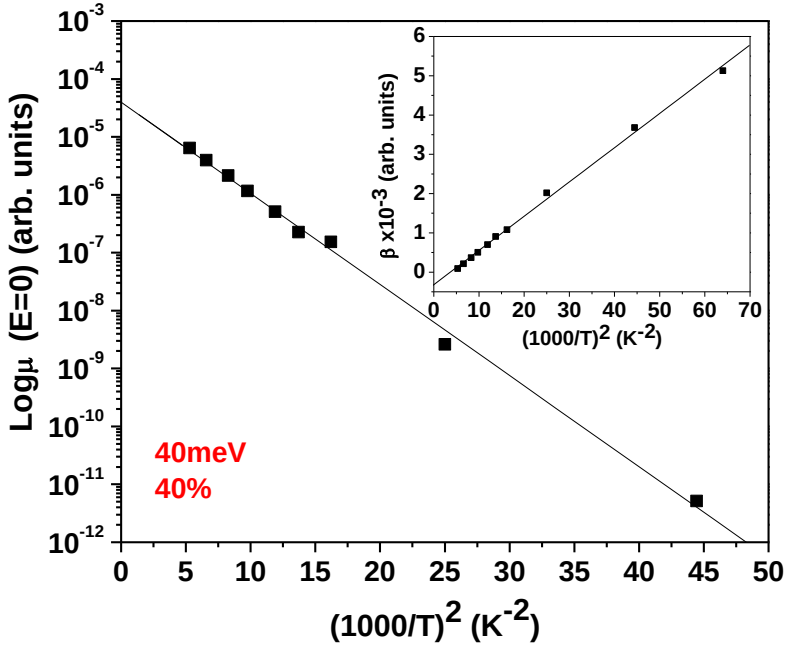
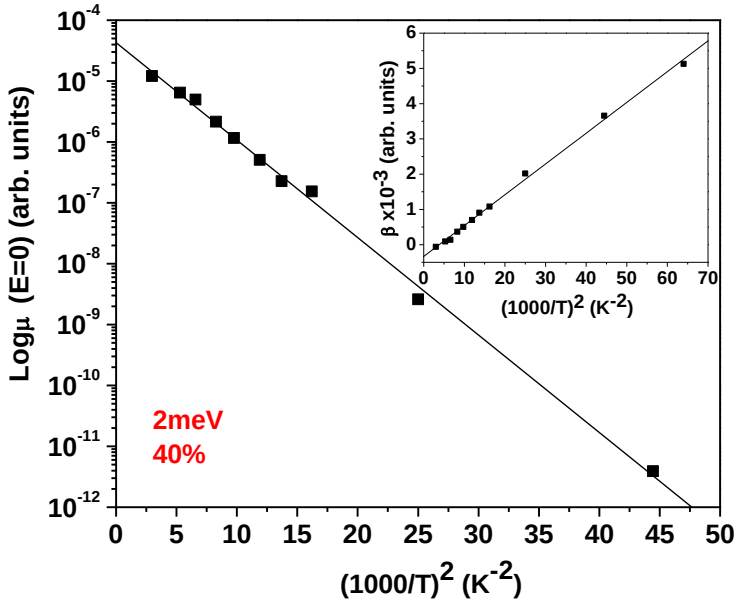
Temperature dependence of mobility







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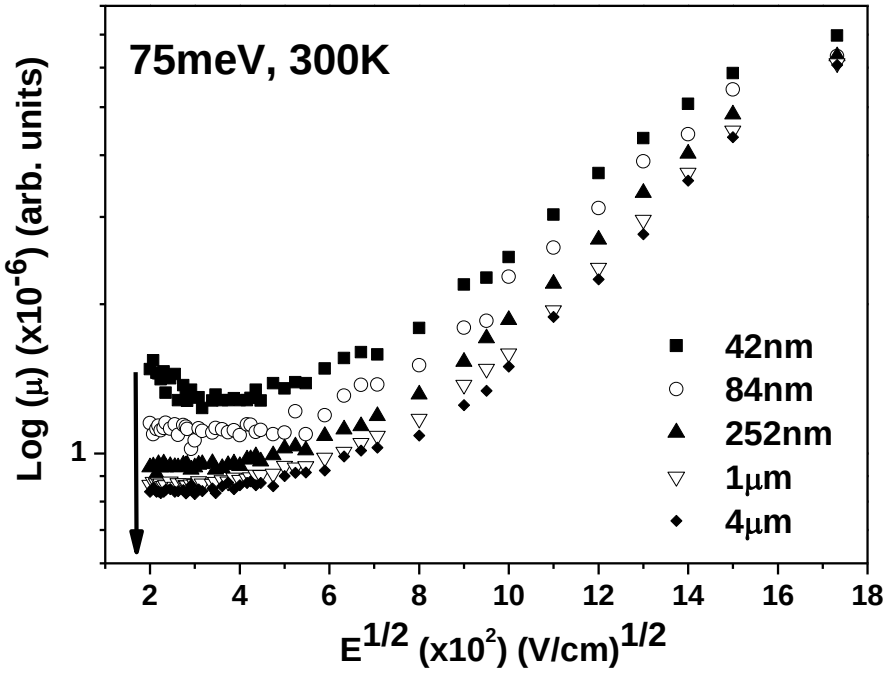
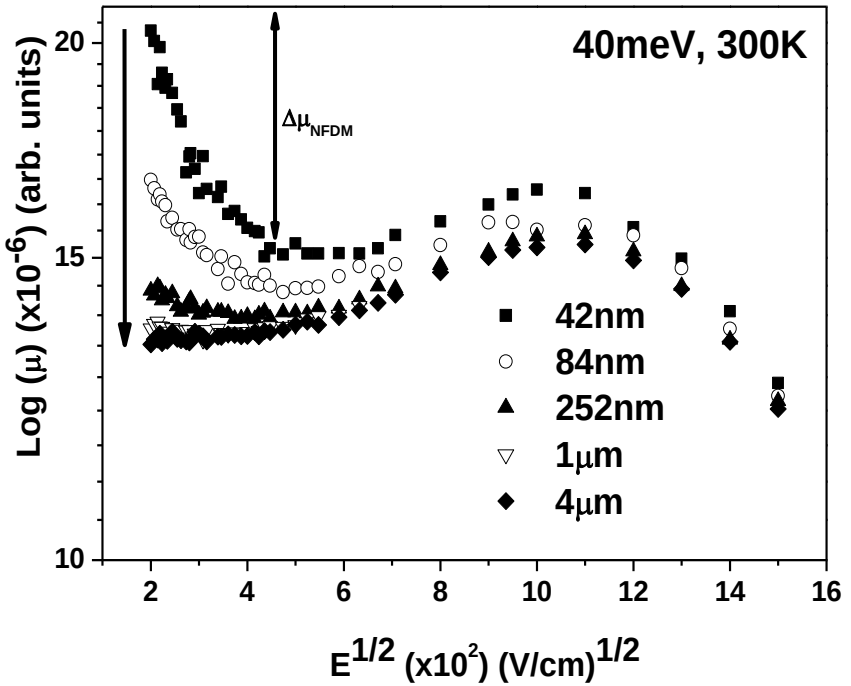
Negative field dependence of mobility at lower thickness

Positional disorder, Σ=0





- While covering larger thickness carrier get more time to relax towards equilibrium energy.

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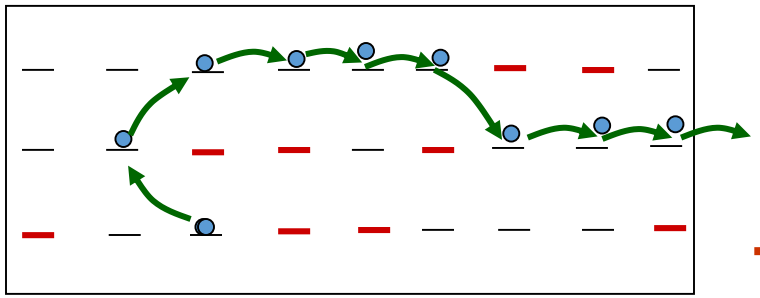
Energetic relaxation of the carriers

Low field



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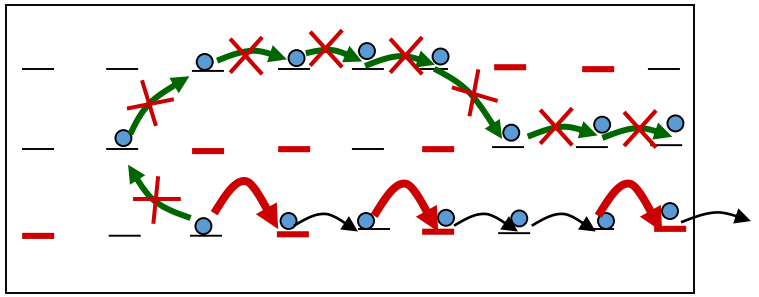
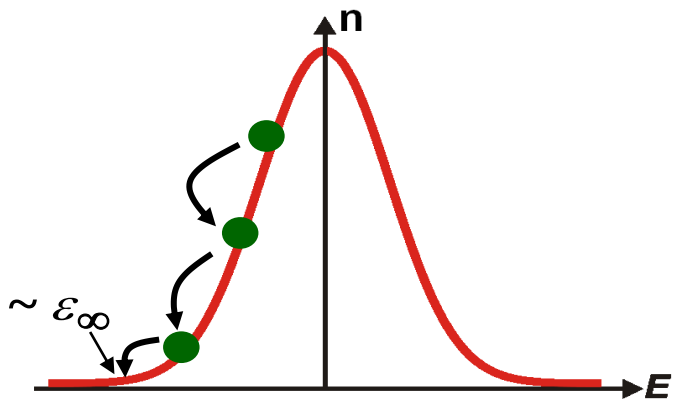
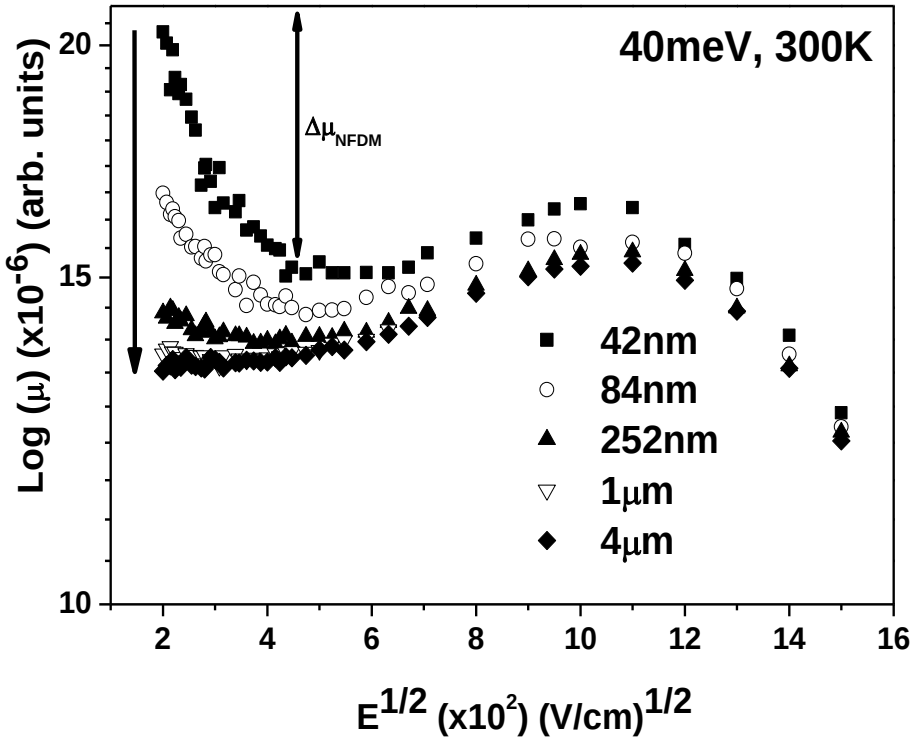
High field



High Energetic Barrier



Decrease in the energy by relaxation reduces the carrier's ability for finding least resistant paths.



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Temperature dependence of NFD mobility

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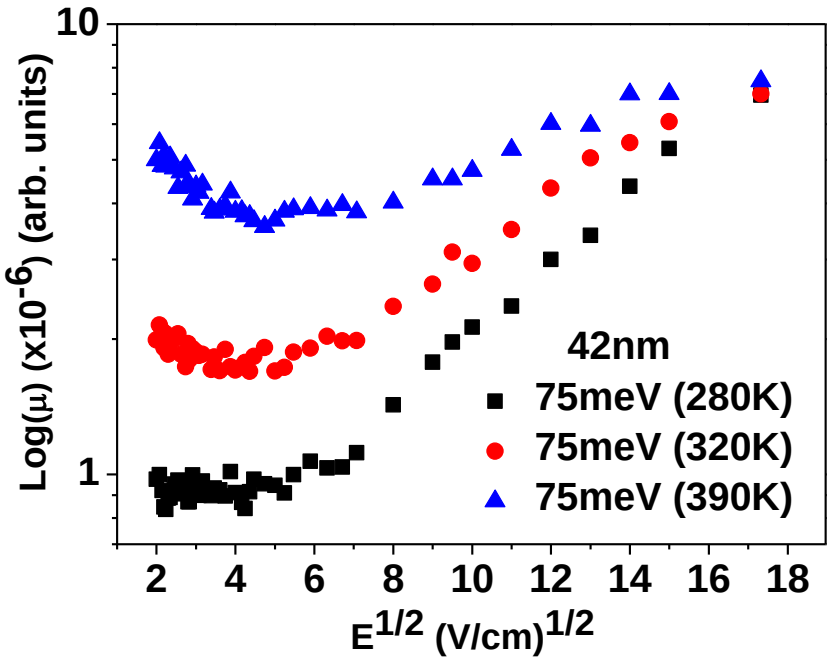
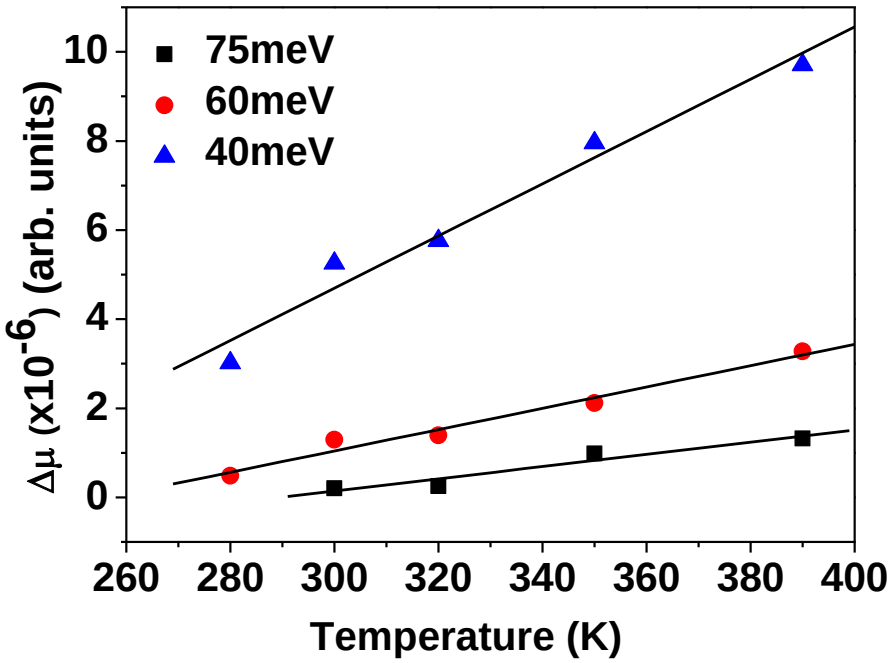


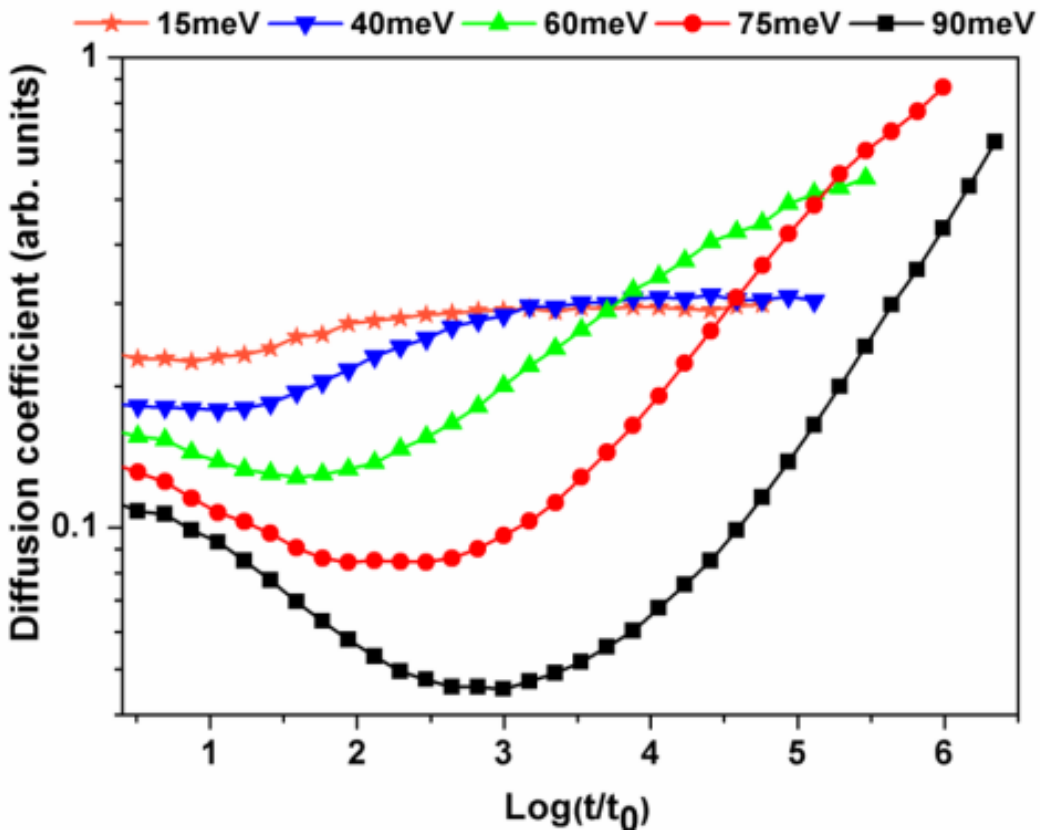


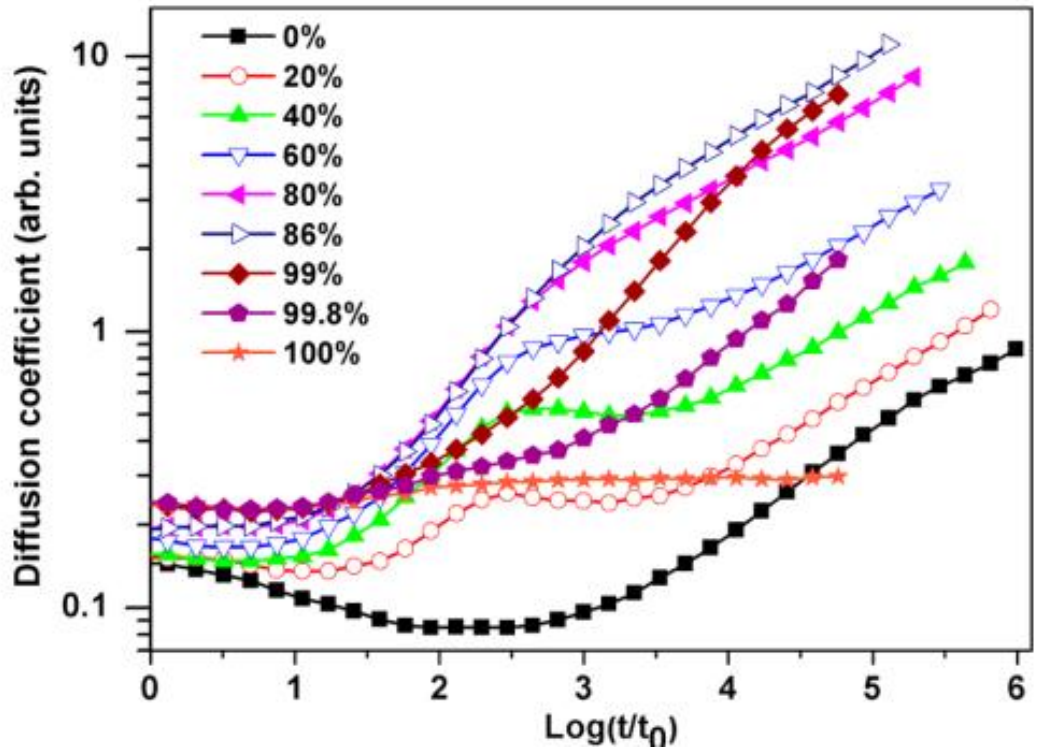
- Carrier gains more thermal energy and hence it can find more number of least resistant paths. Thus a stronger NFDM is expected.

Conclusion

- NFDM can be observed in samples with smaller thickness even in the absence of positional disorder. Explained on the basis of energy relaxation of carrier.
- The study also stresses the possible role of energetic disorder in the origin of NFDM

Diffusion of carrier in homogeneous and inhomogeneous systems





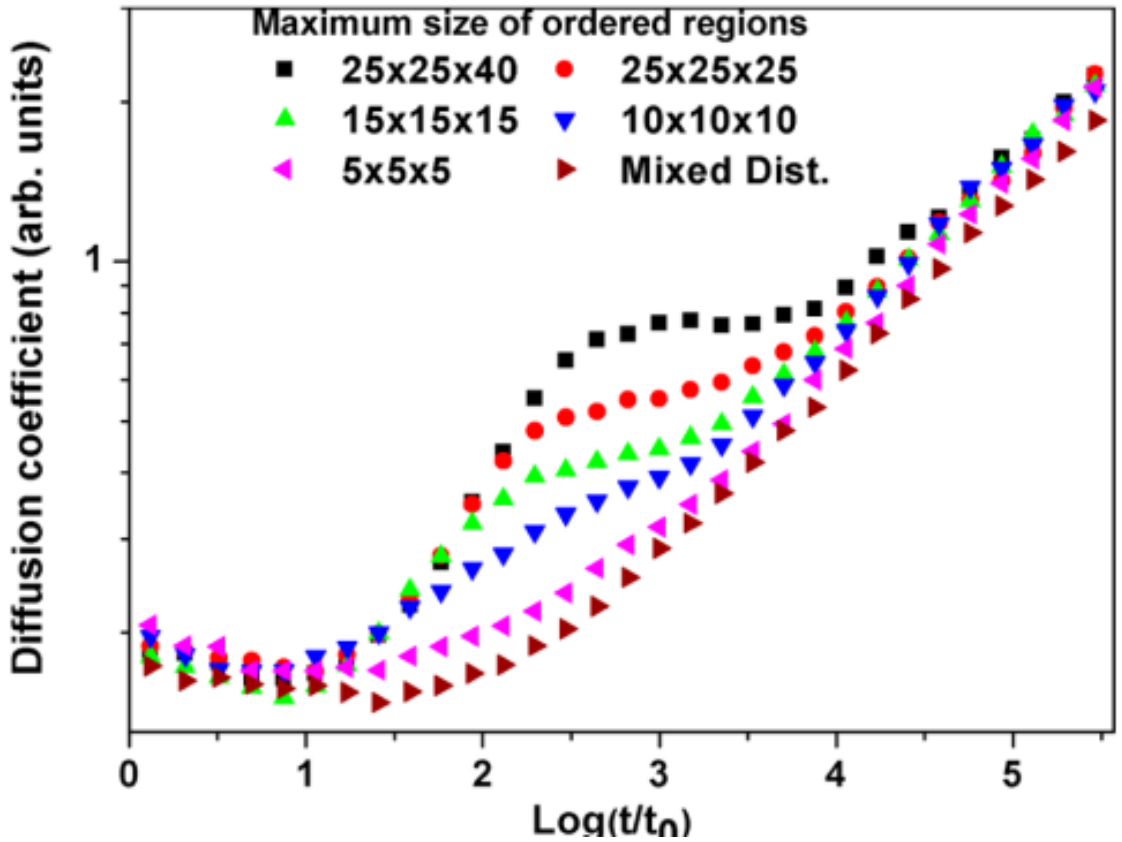
T=300 K, E=6.4X10^5 V/cm; Lattice: 70X70X10000, Averaged
Over 10000 carriers, Maximum Size of ordered region: 25X25X40

Energetic Disorder: 75/15 meV,
mean: 5.1 eV

J. Phys. Chem. C 2013, 117, 24663−24672

Diffusion of carrier in inhomogeneous systems

Dependence of size of ordered regions



COR : 50%

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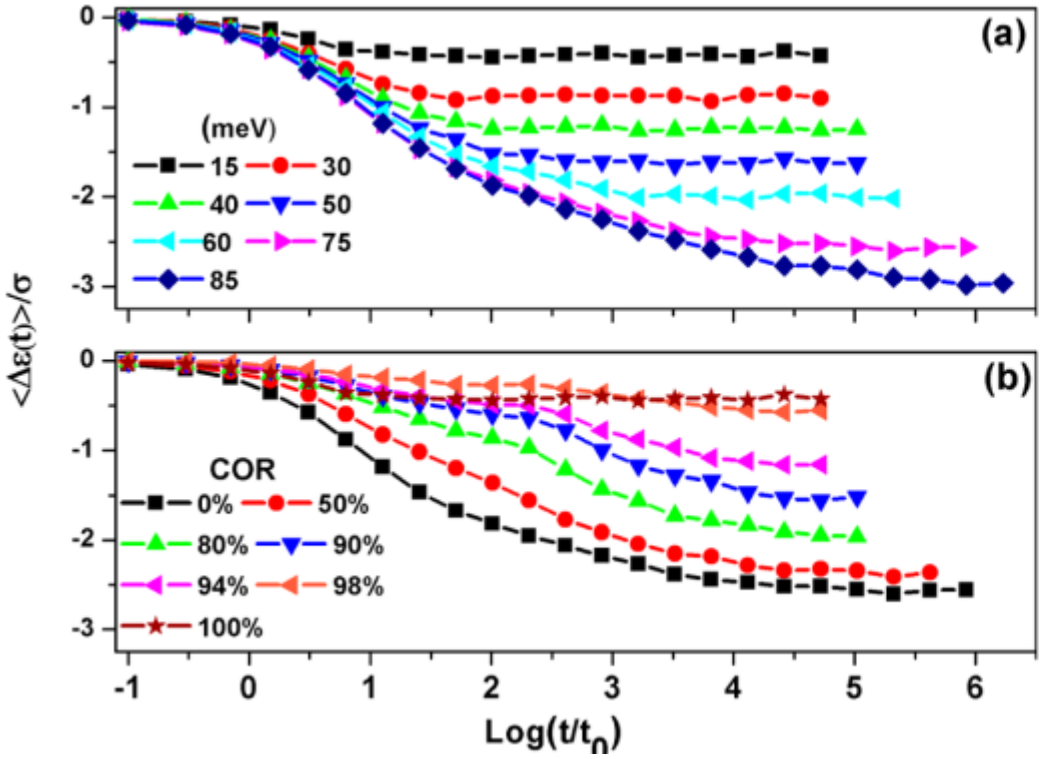
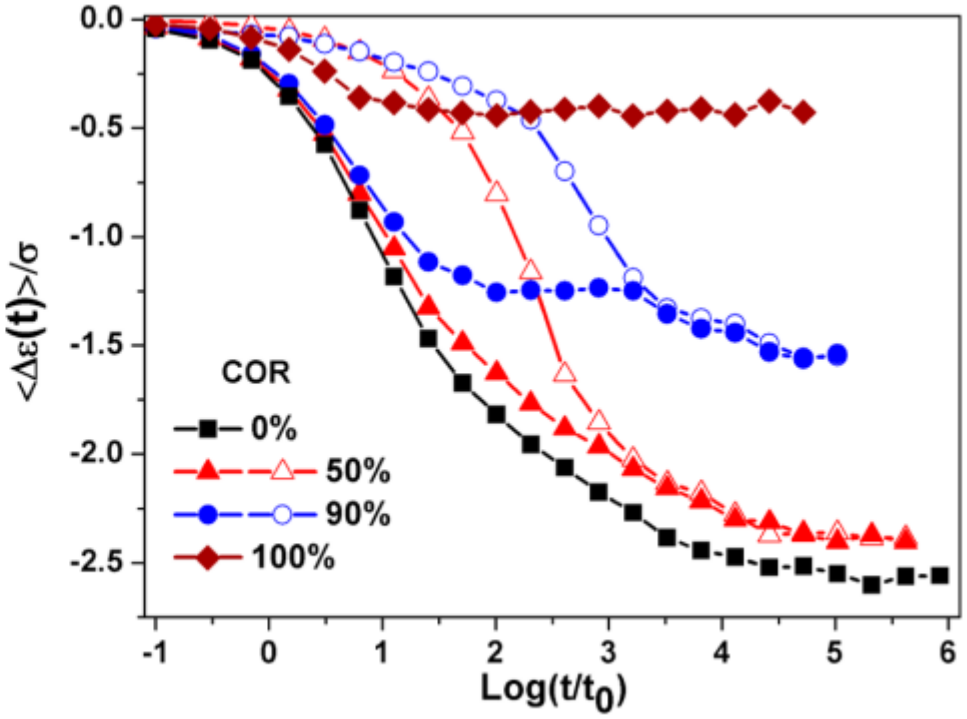
Relaxation of carrier in homogeneous and inhomogeneous systems





Relaxation of Carriers generated in ordered region (open symbols) /disordered region (solid symbols)

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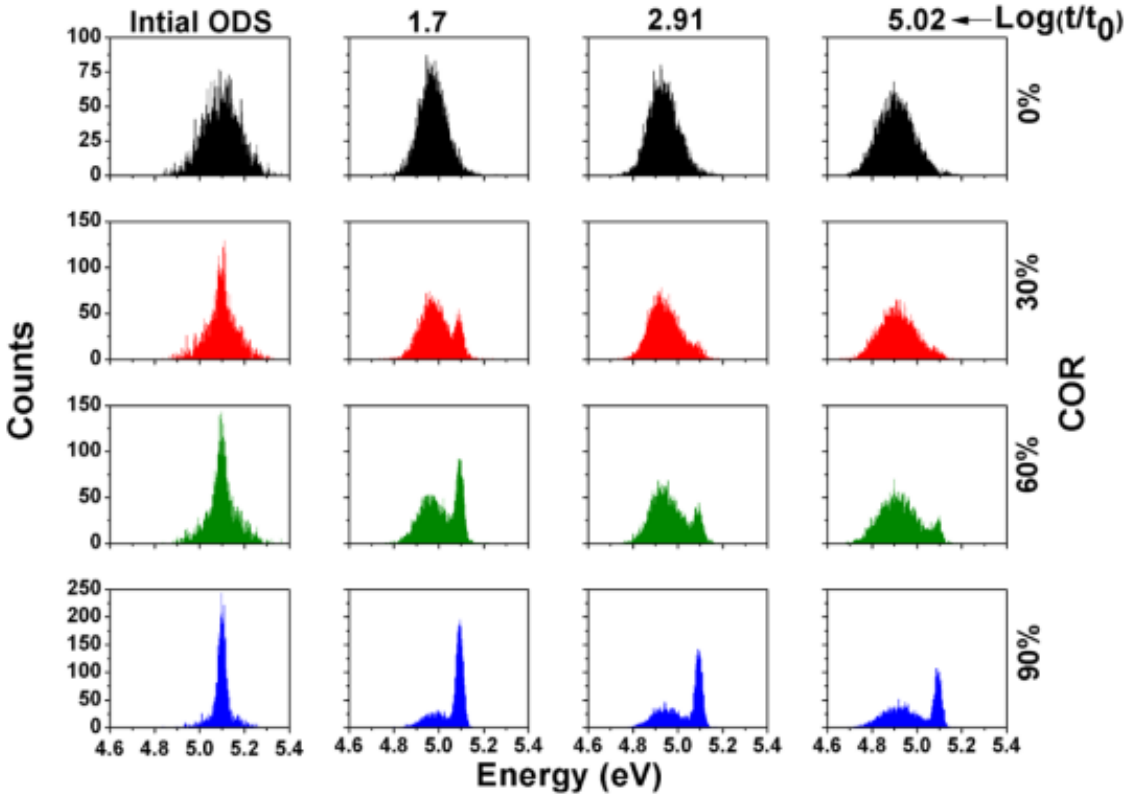
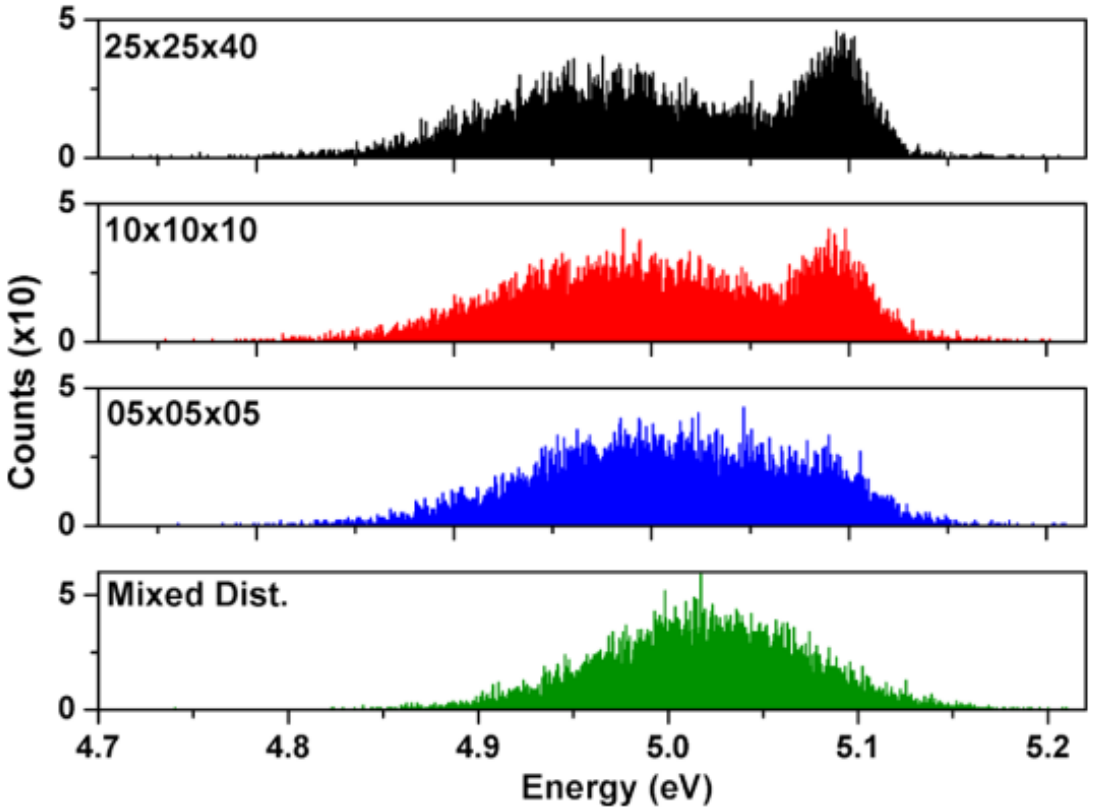
Temporal evolution of the occupation of DOS





COR=50%, log(t/t_0)=1.7

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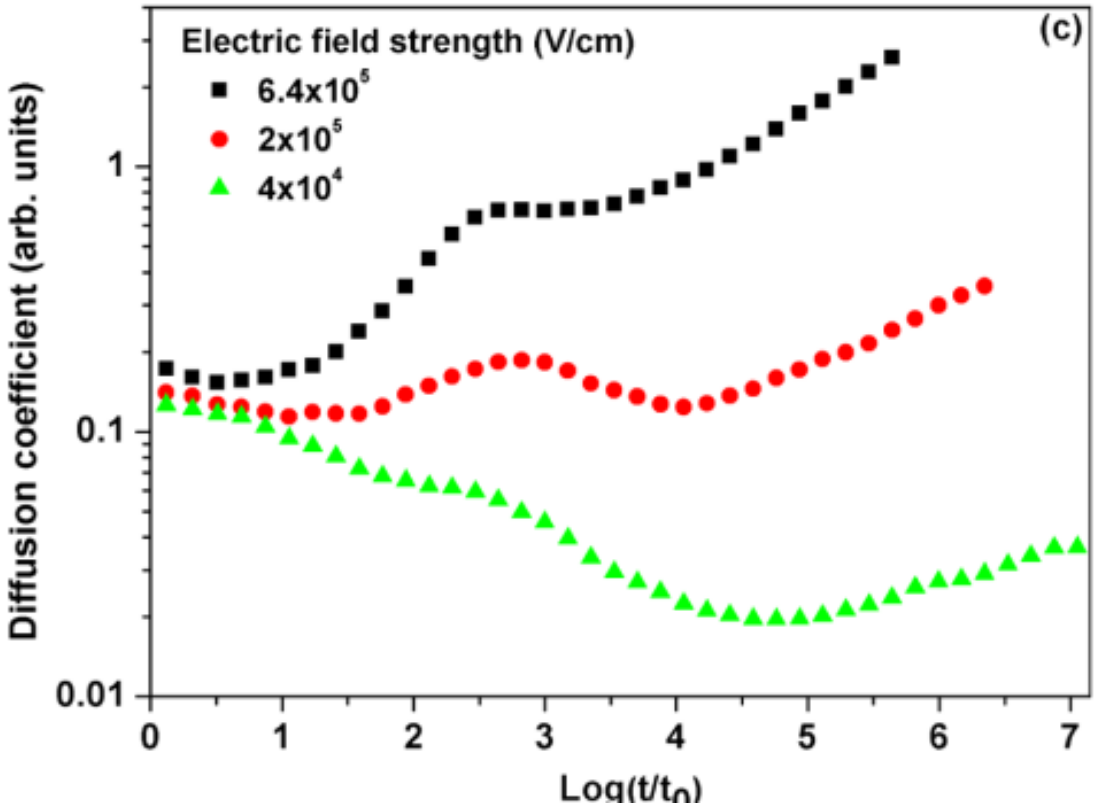
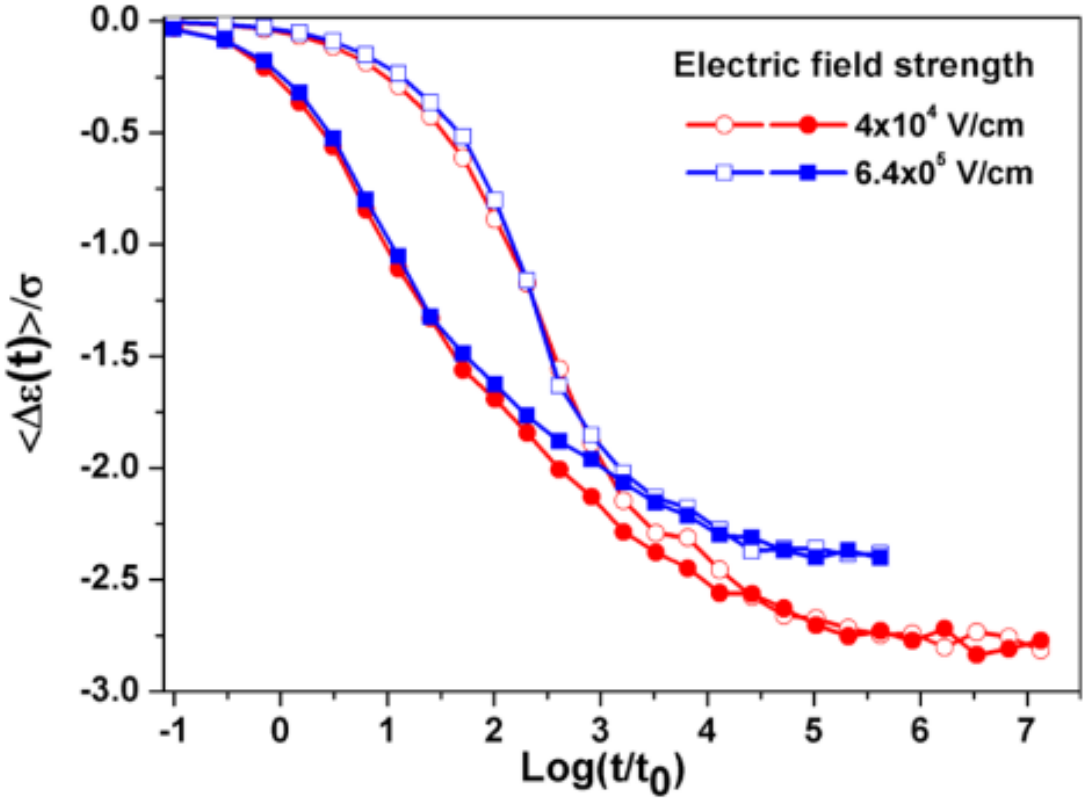
Diffusion of carrier in inhomogeneous systems

Dependence on electric field





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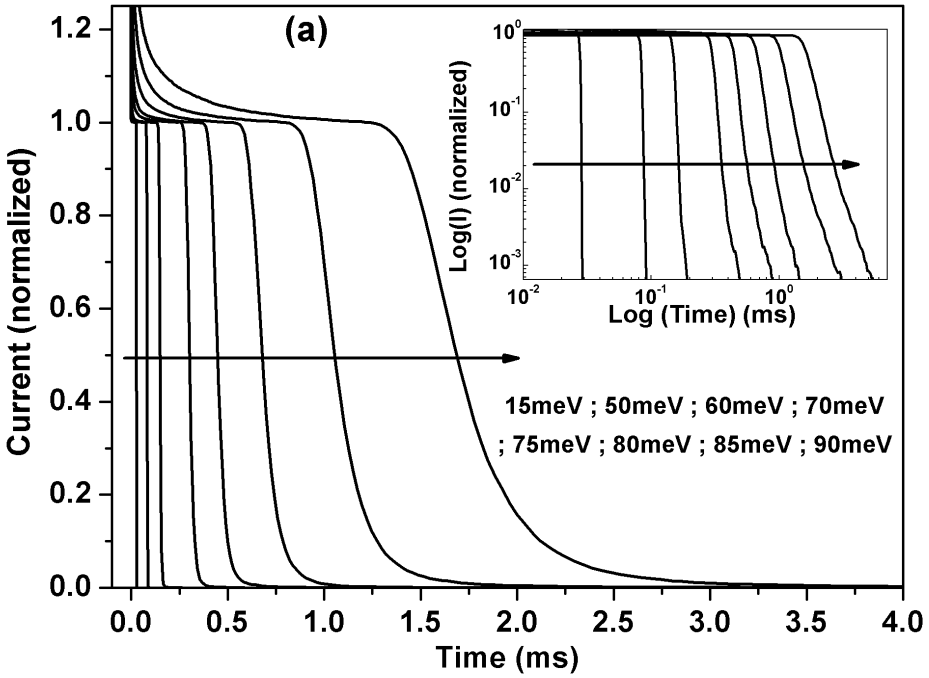
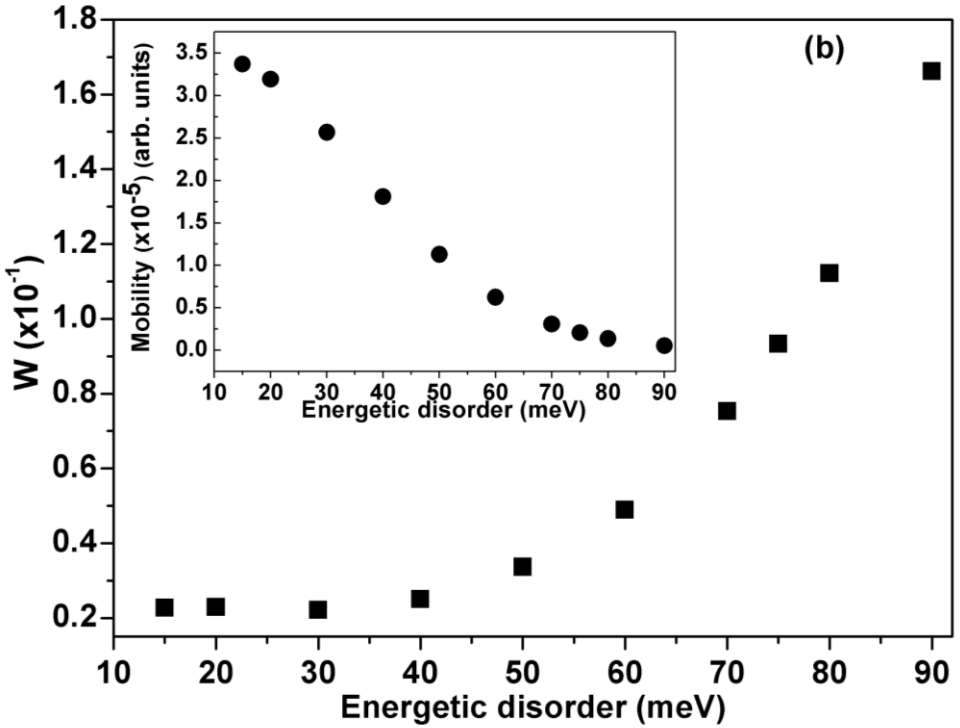
Tail broadening of TOF pulse in homogeneous systems





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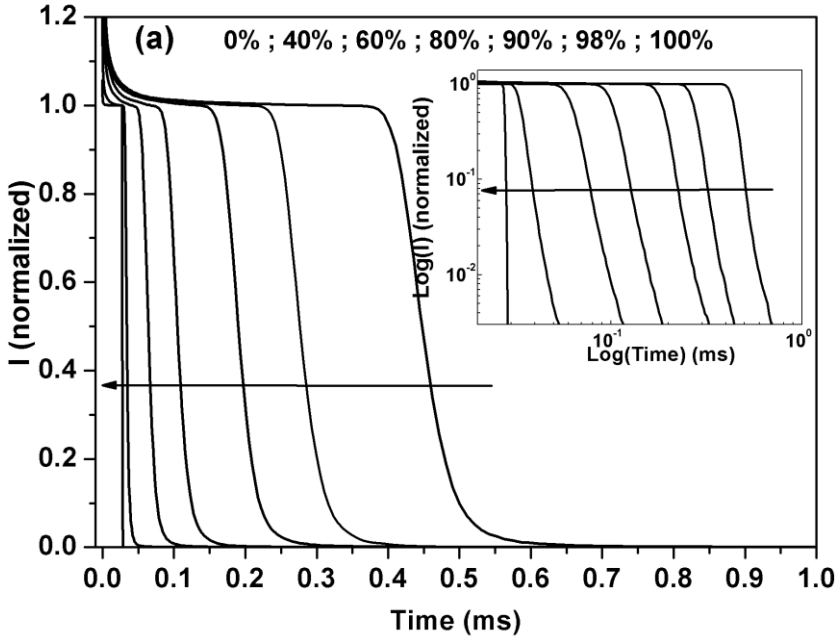
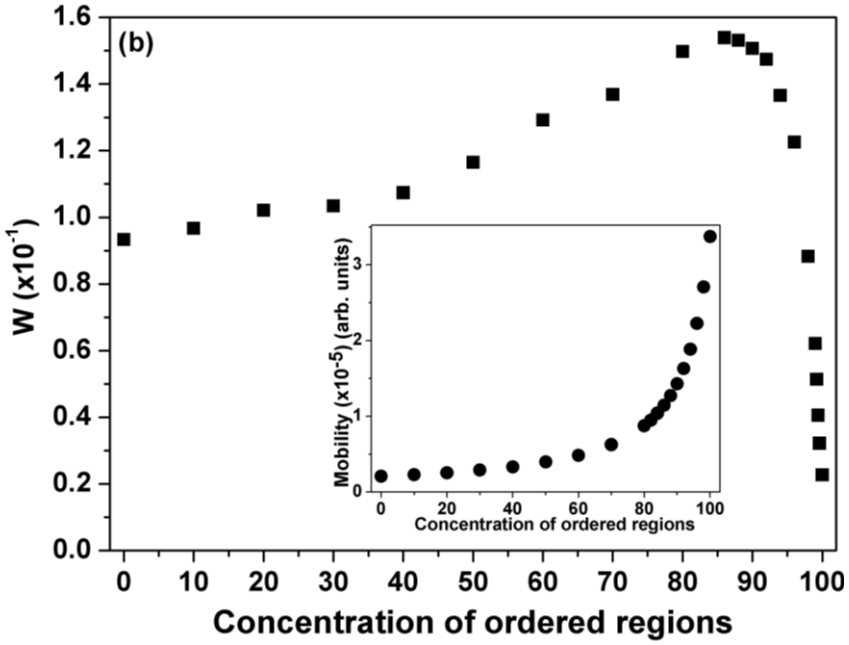
Tail broadening of TOF pulse in inhomogeneous systems





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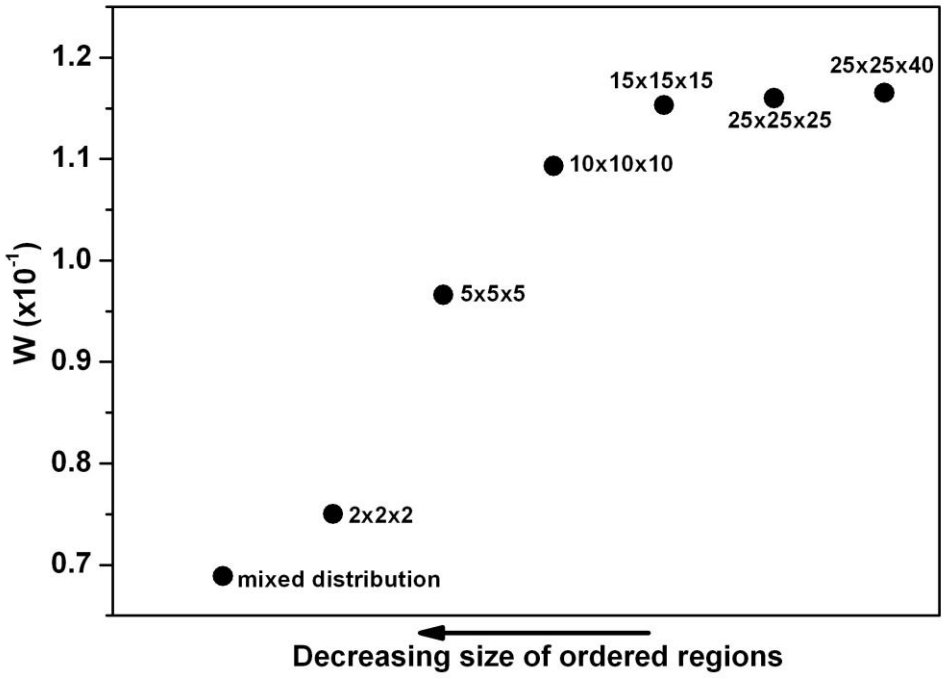
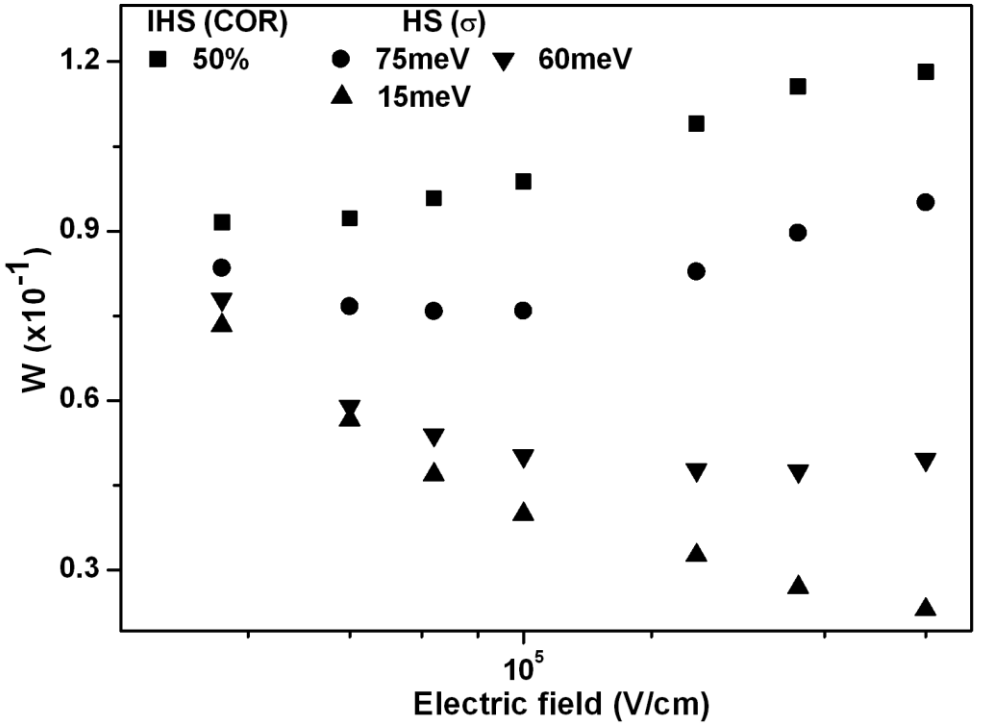
Tail broadening of TOF pulse in inhomogeneous systems

Dependence of size of ordered regions



Dependence on applied electric field



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Conclusion and Outlook

- Morphology and disorder influence the charge transport.
- Interface needs to be modelled correctly
- Effect of positional disorder ?
- Model of charge transport through the ordered region?

Thank you for your attention