Week 1-8

Electronic Properties 2

Energy bands (cont'd)

Charge transfer: hopping

Ohmic and space charge currents

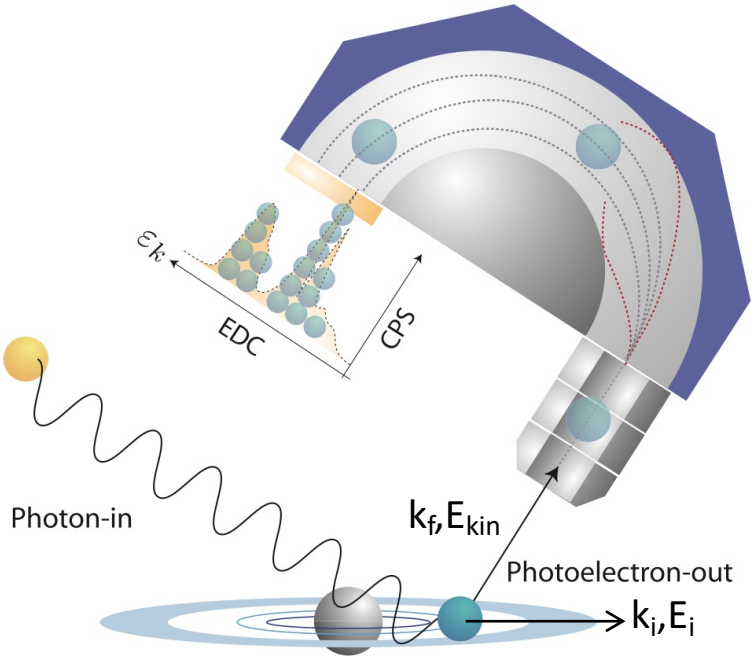
Measuring mobility

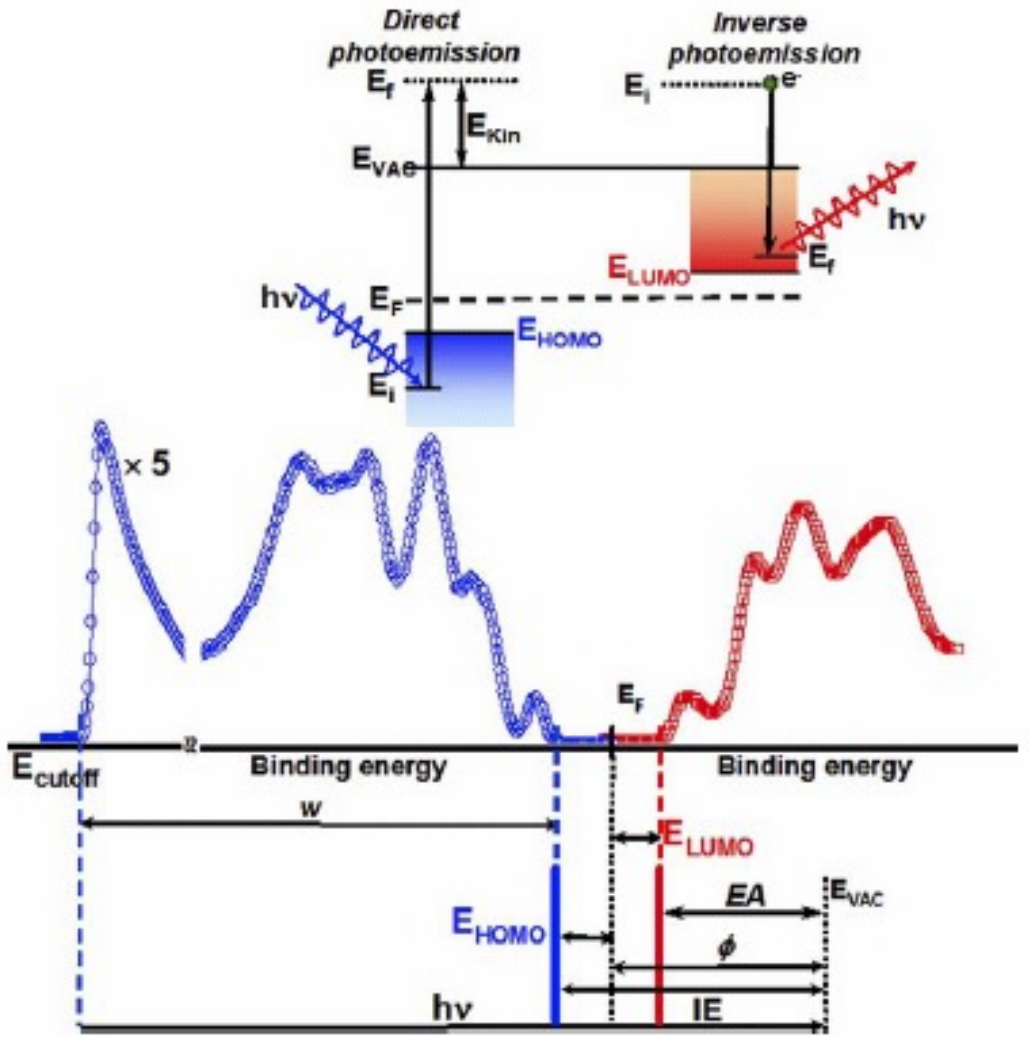
Ch. 4.2-4.4

Measuring Band Structure (and other energies of interest)

- Ultraviolet photoelectron spectroscopy (UPS)

  - Photoelectric effect used to measure energy of a single electron from the HOMO to the vacuum level.
  - Gives *k* of photoemitted electron
  - Varying angle (ARUPS) of sample gives dispersion E(**k**) for $k_\perp$

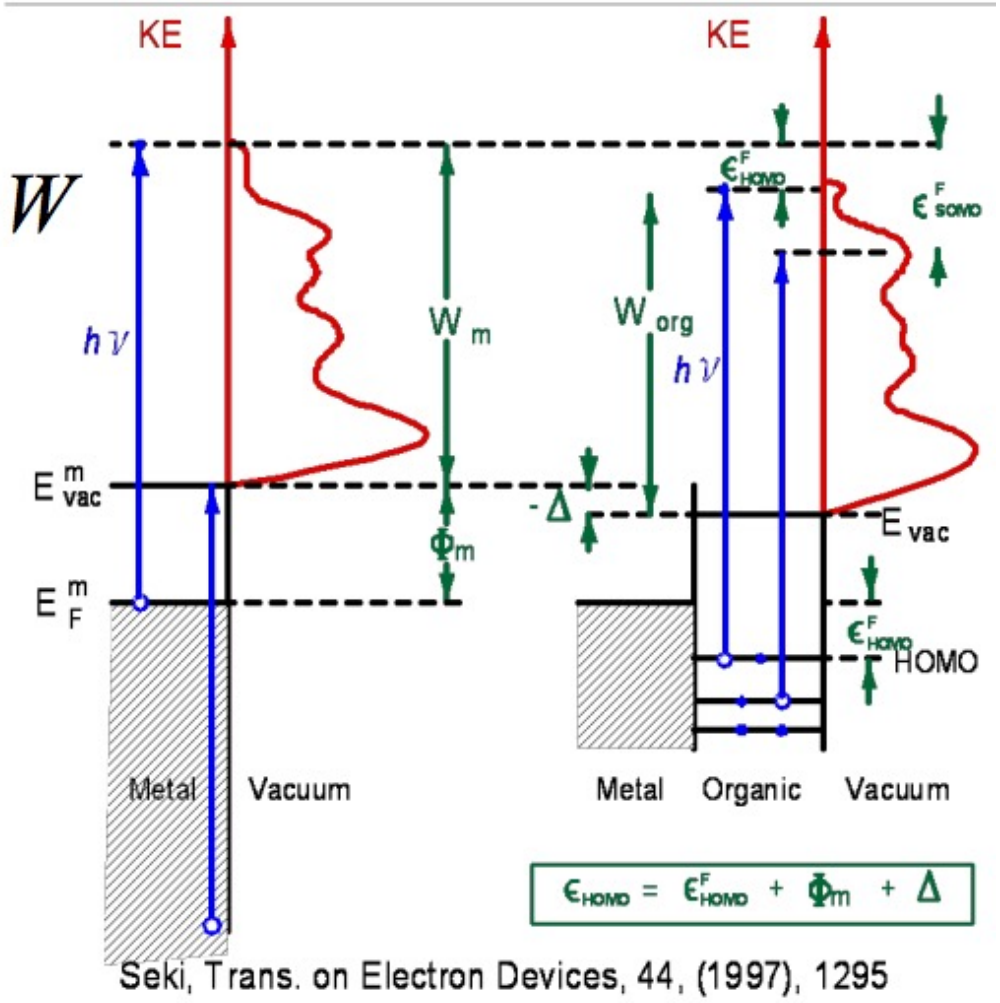




Interpretation of PES Spectra

$$\varphi_m = h\upsilon - W$$

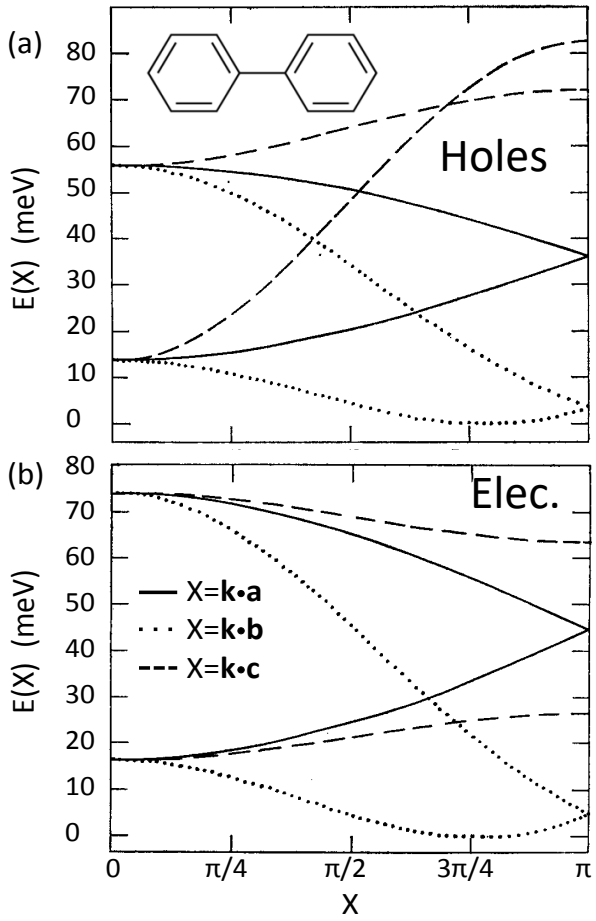
He I = 21.2 eV



Seki, Trans. on Electron Devices, 44, (1997), 1295

SOMO=singly occupied MO

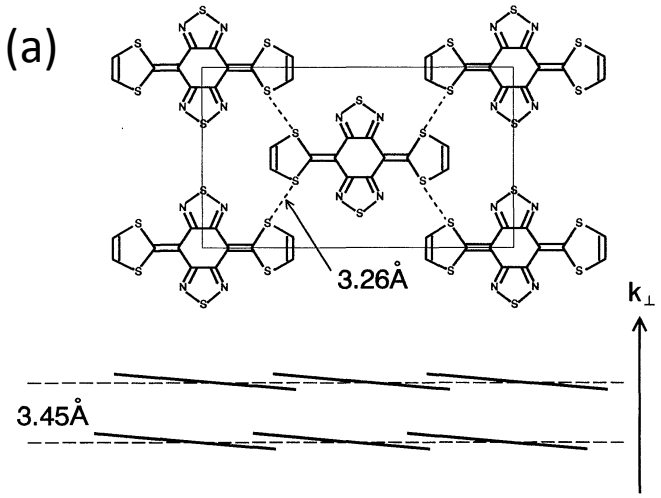
Calculated and Measured Band Structures

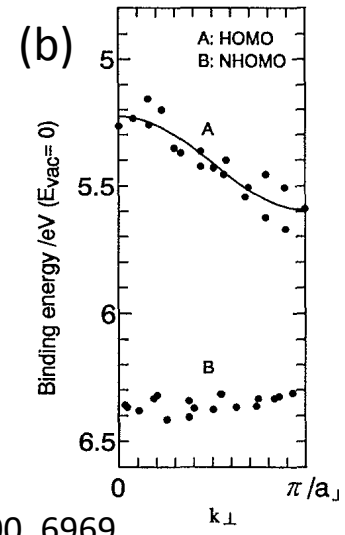


Calculated structure for biphenyl:

- Two molecules/cell give 2 branches *along each direction*
- Max. BW= ~ 70 meV for electrons & holes

Katz, J. I., et al. 1963. *J. Chem. Phys.,* 39**,** 1683.





Hasegawa, S., et al. 1994. *J. Chem. Phys.,* 100**,** 6969.

Measured structure for BTQBT:

- Technique: ARUPS
- Minimum contact distance: 3.26 Å
- HOMO BW = 400 meV
- m* = 3.1 m_0
- Recall: $\mu_h = \frac{q\tau}{m_h^*}$
- But thermally broadened bands have $\tau > \hbar / k_B T$
- μ ~ 6.5 cm^2/V-s (c.f. Hall measurement of 4 cm^2/V-s)

(NHOMO = next highest orbital)

Charge Mobility Describes Transport in Solids

- Charge mobility: μ (not the dipole moment!)

- Definition: Constant of proportionality between velocity and electric field:

$$\mathbf{v}(\mathbf{k}) = \vec{\mu}_{\mathbf{k}}\mathbf{F}$$

  - Tensor: dependent on crystal direction
  - Generally field dependent: $\mu=\mu(\mathbf{F})$
  - Depends on energy dispersion (i.e. band structure) via:

$$\mathbf{v}(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial E(\mathbf{k})}{\partial \mathbf{k}}$$

  - For band-like transport: $\mu = \frac{q\tau}{m^*}$

(τ = mean free scattering time of the charge in the crystal:
For thermally broadened bands: $\tau > \hbar / k_B T$)

- Ohms Law: $\mathbf{j} = q\left(n\mathbf{v}_e + p\mathbf{v}_h\right) = \vec{\sigma}\mathbf{F}$

  - or $\vec{\sigma} = q\left(n\vec{\mu}_e + p\vec{\mu}_p\right)$

Mobility and Charge Diffusion

- Near equilibrium, the Einstein relationship connects these quantities:

$$\frac{D}{\mu} = \frac{k_B T}{q}$$

- Charge diffusion length: $L_q = \sqrt{D\tau}$

Band vs. Hopping Transport

- The charge diffusion length is: $L_q = \sqrt{D\tau} = \left[\frac{\mu\tau k_B T}{q}\right]^{\frac{1}{2}}$
- Band transport occurs when $L_q >> a$.
- From uncertainty: $BW \bullet \tau > \hbar$
- Condition for band conduction $\Rightarrow \mu > \frac{qa^2}{\hbar}\left(\frac{BW}{k_B T}\right)$
  - (Ex. Room temperature, let BW=25 meV, a=5Å. Then μ>5 cm^2/V-s)
- Hopping due to short range interaction involving only nearest neighbor molecules
  - Incoherent diffusive process
  - Electron is heavy since it self traps: it polarizes the neighborhood and must carry that energy along with it.
  - Since only nearest neighbors are affected = **small polaron**
  - Ionic materials, where the interaction goes as ~1/r = **large polaron**

Holstein, T. 1959. Studies of Polaron Motion. Part II. The "Small" Polaron. *Ann. Phys.,* 8**,** 343

Hopping Formalism

- Total Hamiltonian:

$$H_T = H_e^0 + H_{ph}^0 + H_e^{tr} + H_{e-ph}^{loc} + H_{e-ph}^{non} + H_e^{stat}$$

Unperturbed molecule | Electron transfer: *BW ~ J* | Dynamic disorder | Static disorder

- Important terms:

$$H_e^{tr} = \sum_{m \neq n}^{N} J_{nm} a_n^+ a_m$$ $a^+(a)$ = electron creation (annihilation) operator

$$J_{nm} = \left\langle \psi_n(\mathbf{r} - \mathbf{R}_n) \middle| H_e^{tr} \middle| \psi_m(\mathbf{r} - \mathbf{R}_m) \right\rangle$$ Overlap between molecules *m, n*
- As in tight binding, leads to BW

$$\mathcal{N}_i = a_i^+ a_i$$ Number operator

e-phonon coupling constant

$$H_{e-ph}^{loc} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q},j} \sum_{m}^{N} \hbar\omega_{\mathbf{q},j} \left(g_m(\mathbf{q},j) b_{\mathbf{q},j} + g_m^*(\mathbf{q},j) b_{-\mathbf{q},j}^+ \right) a_m^+ a_m$$

q = phonon wavevector
j = phonon branch

On-diagonal dynamic disorder: couples excess electron to molecular vibronic levels

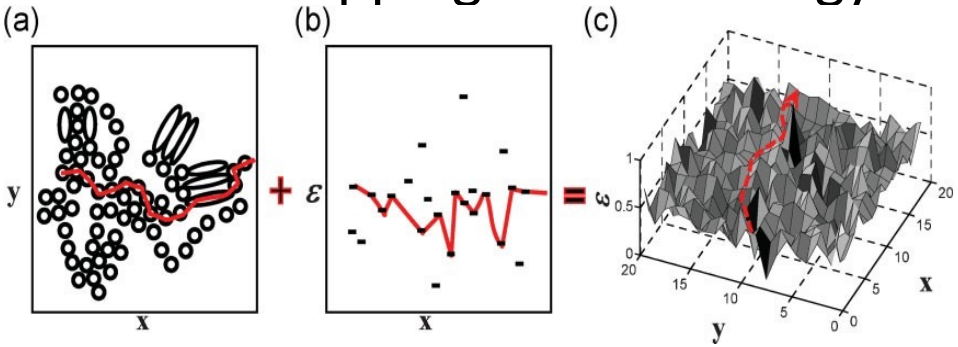
And so on….

The case for static disorder

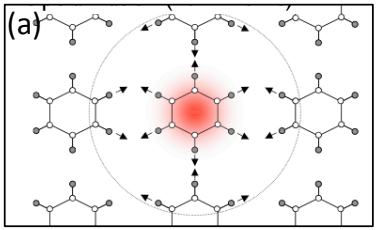
- Most organic semiconductors are permanently disordered
  - Polymers generally not formed into crystals
  - Small molecules used in devices are often amorphous or nanocrystalline
  - Even “perfect” crystals have impurities, stacking faults, dislocations
- A complete picture must include static disorder term:

$$H_e^{stat} = \sum_{n}^{N} \delta\varepsilon_n a_n^{+} a_n + \sum_{\substack{m,n \\ m \neq n}}^{N} \delta J_{nm} a_n^{+} a_m$$

- Static disorder leads to hopping in both energy and space.



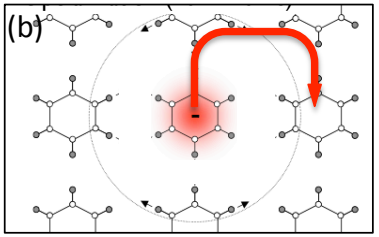
Visualizing Lattice Distortions



Unperturbed molecule

$H_e^0 + H_{ph}^0$

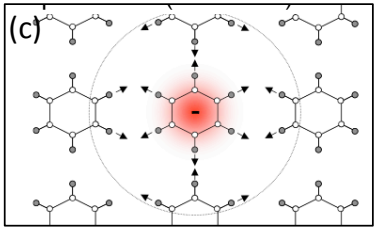
$\varepsilon_n^0;\ \hbar\omega_{\mathbf{q},j}$



Electron transfer

H_e^{tr}

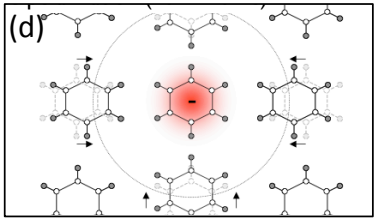
J_{nm}



*Intra*molecular phonons

H_{e-ph}^{loc}

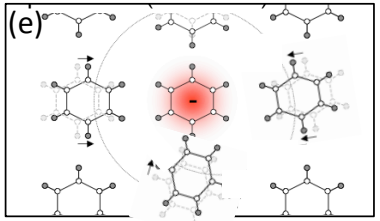
$g_m(\mathbf{q},j)$



*Inter*molecular phonons

H_{e-ph}^{non}

$g_{nm}(\mathbf{q},j)$



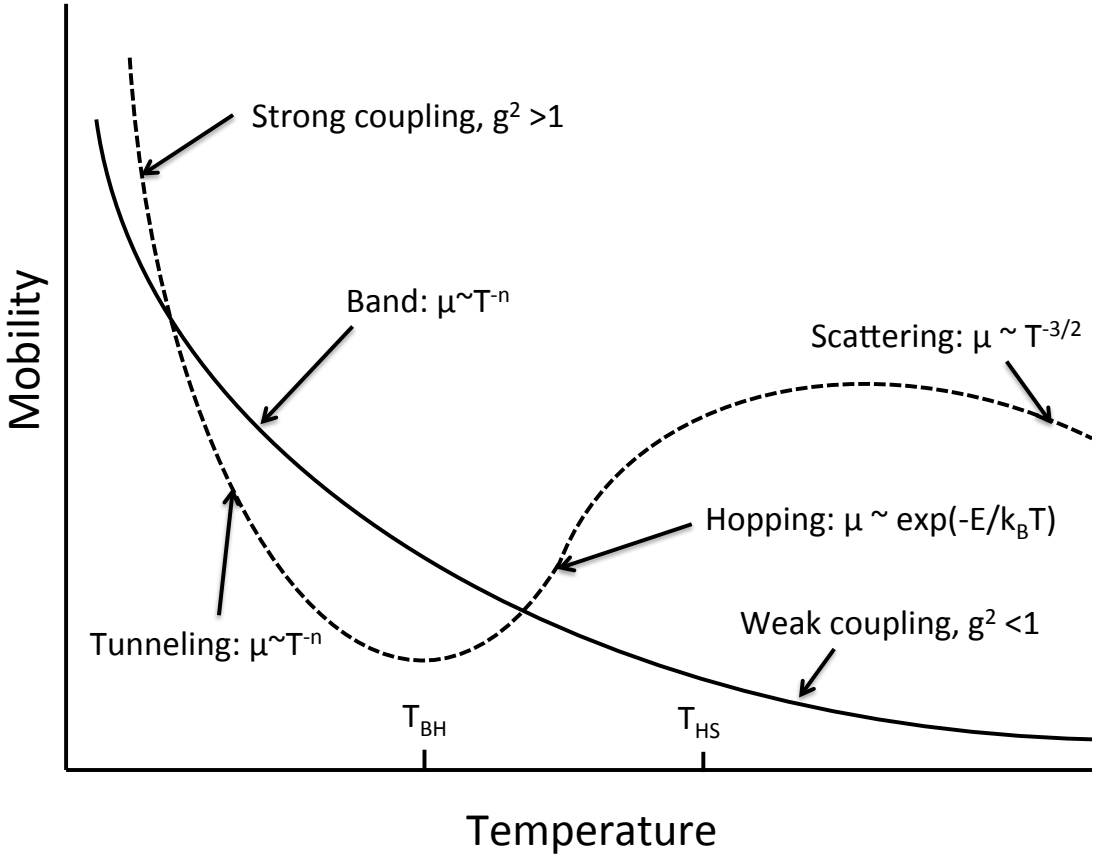
Static disorder

H_e^{stat}

$\delta\varepsilon_n;\ \delta J_{nm}$

Small polaron theory predicts several transport regimes

- Dependent on coupling strength, *g*
- Static disorder not included here
- Band and tunneling both coherent and follow power law dependence



Going from formal theory to a practical quantity (μ)

- Diffusion constant is calculated from hops from site *p*: $p \rightarrow p \pm 1$
- Then in 3D: $D = \frac{1}{3} k_{ET}(p \rightarrow p \pm 1)\frac{a^2}{2}$ (6 sites to choose from on a cube)
- It follows from Einstein: $\mu = \frac{q}{3k_B T} k_{ET}(p \rightarrow p \pm 1)\frac{a^2}{2}$
- From small polaron theory we obtain k_{ET} (remember Fermi's Golden Rule!)
- And with Holstein's help, in the high temperature limit ($k_B T > \hbar\omega_0$):

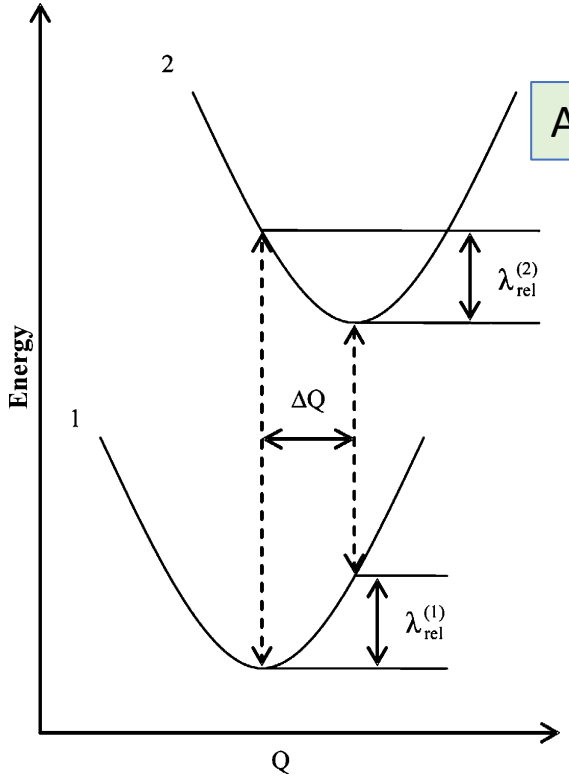
$$\mu_{hop} = \frac{qJ^2 a^2}{6k_B T\hbar}\left[\frac{\pi}{2E_{pol}k_B T}\right]^{1/2} \exp\left(-\frac{E_{pol}}{2k_B T}\right)$$

- ✓ The hopping mobility is thermally activated
- ✓ It scales with the square of the bandwidth, J^2.
- ✓ As E_{pol} increases, μ_{hop} decreases
- ✓ As $T \rightarrow$ large; then $\mu_{hop} \sim T^{-3/2}$: scattering!
- As $T \rightarrow$ small; then μ_{hop} replaced by μ_{tun}

Molecular energy changes when a charge is transferred

The effects of polarization (small polaron theory)

Molecular relaxation due to polarization: analogous to FC for excitons



Assume identical molecules at *i* and *f*

Charged state

Neutral ground state

Reorganization energy: $\lambda_{reorg} = \lambda_{rel}^{(1)} + \lambda_{rel}^{(2)}$

Or polarization energy ≈ $E_{pol}^{loc} = \lambda_{reorg} / 2.$

Description of Hopping + Disorder

- Master equation for a site at $\mathbf{R}_i$ being occupied at time, t:

$$\frac{\partial f_i(t)}{\partial t} = \sum_{j\neq i}^{N}\left\{-k_{ij}f_i(t)\left[1-f_j(t)\right]+k_{ji}f_j(t)\left[1-f_i(t)\right]\right\}-k_{rec}f_i(t)$$

Jump rate from i➔j

Prob. of jump from i➔j

Prob. of jump from j➔i

Prob. for recombination

- $f_i(t)$ is described by Fermi-Dirac statistics, but this is complicated.
- Simplifications:
  - At low densities, terms in f_i^2 can be ignored
  - Assume no recombination between hopping events (k_{rec}=0).

$$\Rightarrow \frac{\partial f_i(t)}{\partial t} = \sum_{j\neq i}^{N}\left\{-k_{ij}f_i(t)+k_{ji}f_j(t)\right\}$$

- Current is then found by:

Density of states of hopping sites

$$j_{+x}(t) = q\int \rho(\varepsilon)\,d\varepsilon \sum_{i}^{N}\left[\frac{\partial f_{i,+x}(\varepsilon,t)}{\partial t} - \frac{\partial f_{i,-x}(\varepsilon,t)}{\partial t}\right]$$

The theory of μ

- **Goal:** To find μ, but now with disorder expressed through $\rho(\varepsilon)$.
- We first need to find the rates, k_{ij} in the presence of disorder.
  - **Model 1: Miller-Abrahams theory**
    - Developed for impurity band conduction in semiconductors
    - Valid for weak electron-phonon coupling (g_m, g_{nm} small)

$$k_{ij} = \upsilon_0 \exp\left(-2\gamma_{ij} R_{ij}\right) \begin{cases} \exp\left(-\dfrac{\varepsilon_j - \varepsilon_i}{k_B T}\right) & \varepsilon_j > \varepsilon_i \\ 1 & \varepsilon_j < \varepsilon_i \end{cases}$$

υ_0= hopping attempt freq.~opt. phonon freq.
γ=overlap factor, decay of wavefunction between i,j.
R_{ij}=hopping distance

- Implications:
  - "Uphill" transfers are thermally activated
  - "Downhill" transfers encounter no barrier
  - Valid when $\varepsilon_j - \varepsilon_i < \Theta_m$ (Debye energy) of acoustic and optical phonons (~0.15 eV) $\Rightarrow$ low temperatures
  - In F-field, add in $-q\mathbf{r}\bullet\mathbf{F}$ to exponential argument where F points from $j \Rightarrow i$

Miller, A. & Abrahams, E. 1960. *Phys. Rev.,* 120**,** 745.

Model 2: Marcus Transfer

- Developed for understanding transfer of electron from donor to acceptor in solution

  - Generalized form of mobility in the small polaron (non disordered) model. Starting point will again be from Holstein:

$$k_{ET} = \frac{6k_B T\mu}{qa^2} \times \frac{J^2}{\hbar}\left[\frac{\pi}{2E_{pol}k_B T}\right]^{1/2} \exp\left(-\frac{E_{pol}}{2k_B T}\right)$$

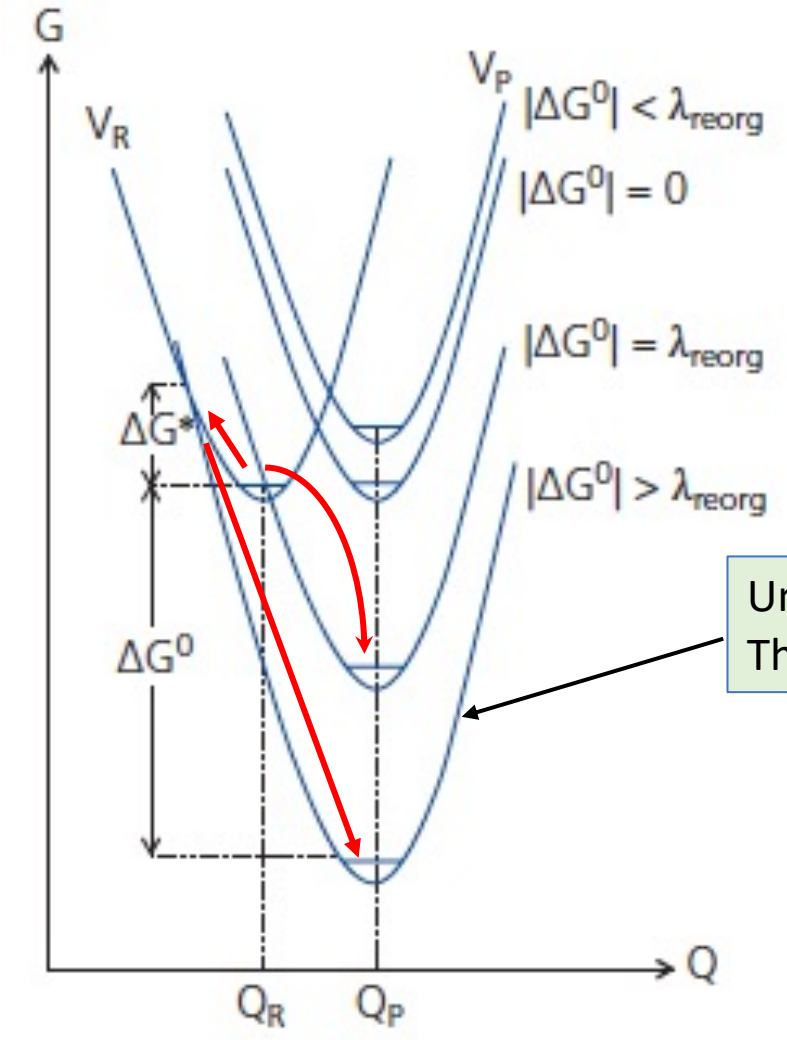
  - Valid for both upward and downward jumps: Only based on difference in free energy between initial and final states, ΔG.
  - Valid at high temperatures, and strong electron-phonon couplings
  - Activation energy for the transfer reaction: $2E_{act} = E_{pol} = \lambda_{reorg}/2$
  - From Miller-Abrahams:

$$J = J_0 \exp\left(-\gamma_{ij} R_{ij}\right)$$

Marcus, R. A. 1993. *Rev. Modern Phys.,* 65**,** 599.

Transfer regimes under Marcus

Transfer rate depends on ΔG which can be less than or greater than 0.



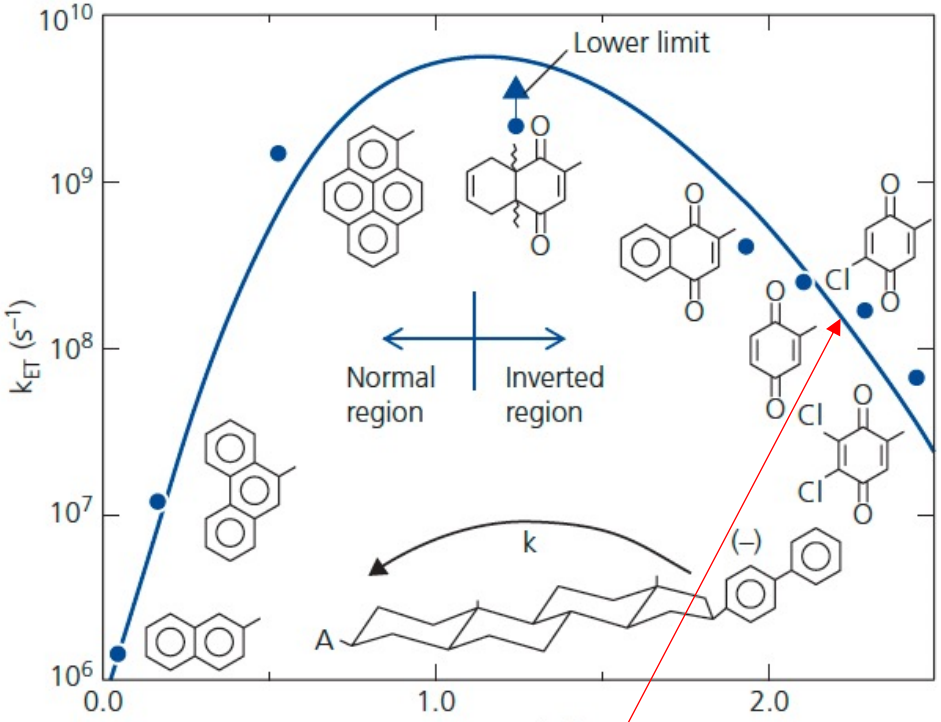
Unique prediction of Marcus theory:
The inverted regime where $|\Delta G_0| > \lambda_{reorg}$

$$k_{ET} = A\exp\left[-\frac{\Delta G^*}{k_B T}\right] = A\exp\left[-\frac{\left(\lambda_{reorg} + \Delta G^0\right)^2}{4\lambda_{reorg} k_B T}\right]$$

Reaching the Inverted Region

Two examples

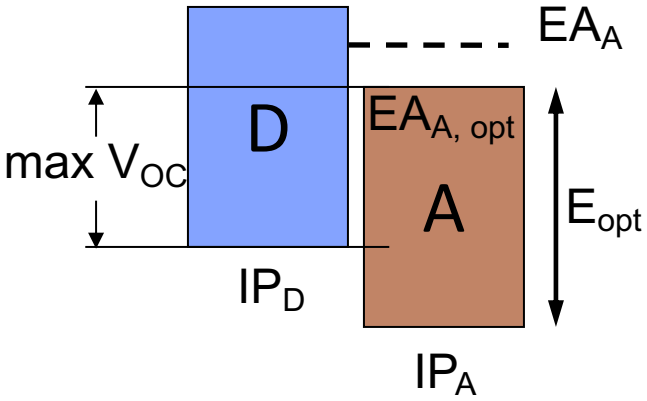
Reaction chemistry across a bridging (Sp) molecule



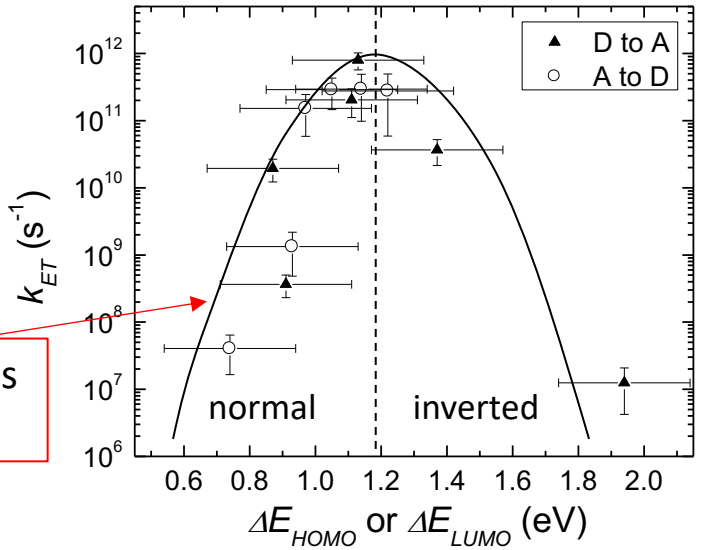
$$A-Sp-B \xrightarrow{-q} A-Sp-B^{-} \underset{k_{-ET}}{\overset{k_{ET}}{\rightleftharpoons}} A^{-}-Sp-B$$

Miller et al., J. Am. Chem. Soc., 106, 3047 (1984)

Charge transfer at an OPV Donor/Acceptor HJ



Predictions of Marcus theory

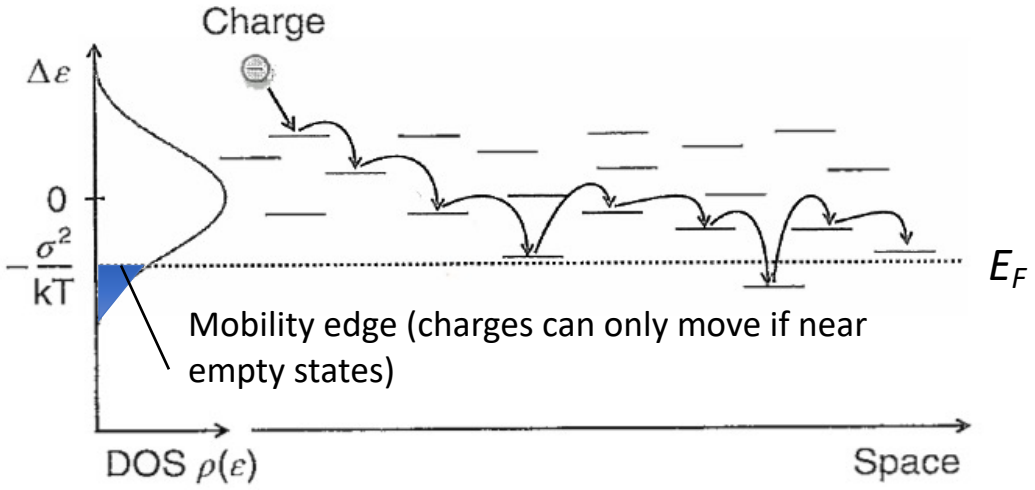


Electron transfer for $D \rightarrow A$ or $A \rightarrow D$

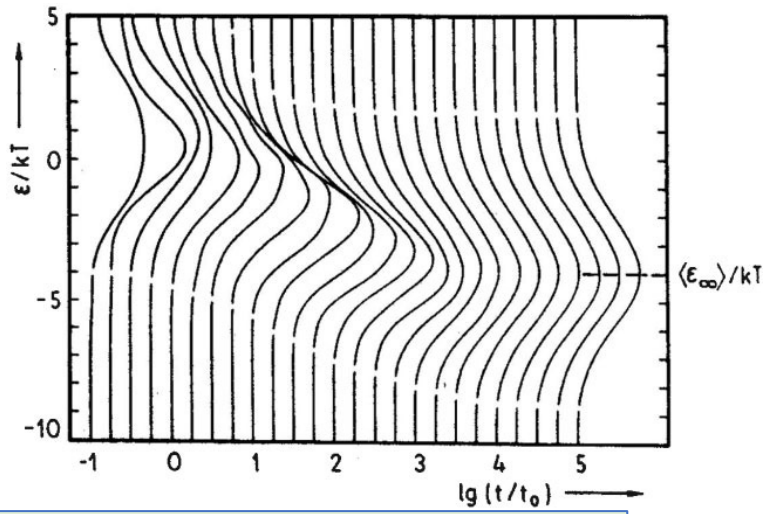
Rand, et al. 2007. *Phys. Rev. B,* 75**,** 115327.

Density of States and the Mobility Edge

Relaxation of a hot carrier



Charge relaxes to ε_∞



A commonly used model: Gaussian Disorder Model (GDM) introduced by Bässler

DOS: $\rho(\varepsilon) = \frac{N_V}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(\varepsilon-\varepsilon_0)^2}{2\sigma^2}\right]$ (consequence of the central limit theorem)

$$\langle \varepsilon_\infty \rangle = \frac{\int_{-\infty}^{\infty} \varepsilon\rho(\varepsilon)\exp(-\varepsilon/k_BT)d\varepsilon}{\int_{-\infty}^{\infty} \rho(\varepsilon)\exp(-\varepsilon/k_BT)d\varepsilon} = -\frac{\sigma^2}{k_BT}$$

Mean equilibrium carrier energy—
Charges relax into the tail of the distribution

Mobility (at last!)

- We now have everything we need:
  - Site occupation: $f_i(\varepsilon)$ from Fermi statistics
  - Transfer rate: k_{ij}
  - Site DOS: $\rho(\varepsilon)$
- As seen previously, mobility depends on k: $\mu = \frac{q}{3k_BT} k_{ET}(p \to p \pm 1)\frac{a^2}{2}$
- But this is not possible to solve exactly.
- Based on Marcus theory (most applicable), including electric field effects we get (ouch!):

$$\mu \approx \mu_0 \exp\left\{-\frac{E_{act}}{k_BT} - \frac{1}{8q^2}\left(\frac{\sigma}{k_BT}\right)^2 + \frac{1}{2\sqrt{2}q^2}\left[\left(\frac{\sigma}{k_BT}\right)^{3/2} - \left(\frac{\sigma}{k_BT}\right)^{1/2}\right]\sqrt{\frac{qaF}{\sigma}}\right\}$$

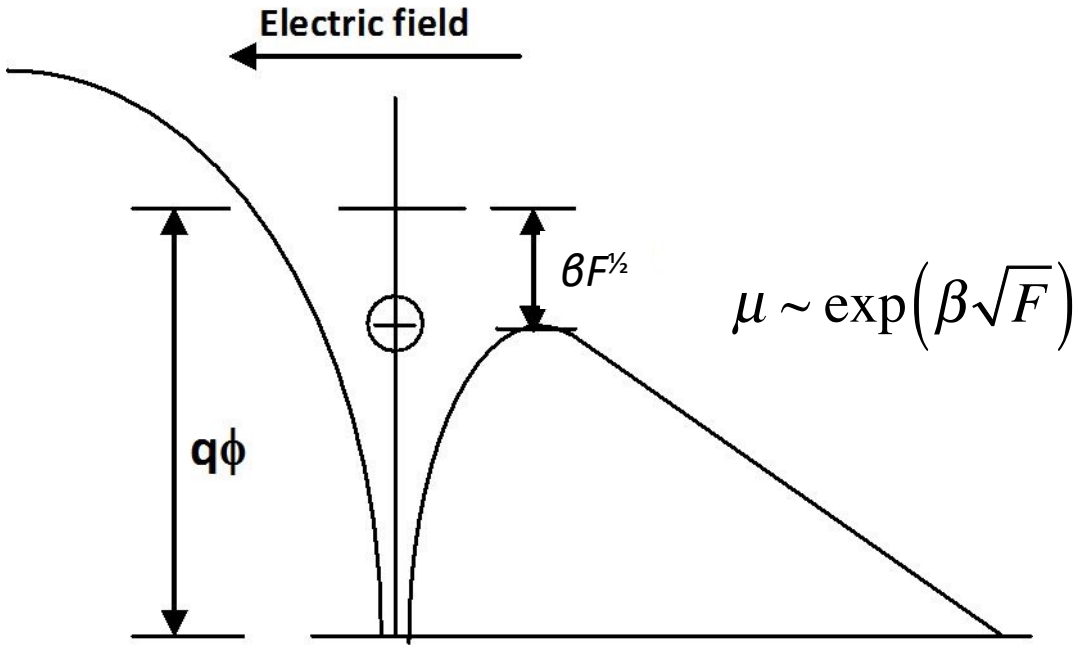
Poole-Frenkel type dependence

- At F=0, mobility activation ~ $1/T^2$ at low T, $1/T$ at high T
- Recall polaronic dependence follows ~$1/T$
- Monte-Carlo simulations show similar form

Fishchuk, I., et al. 2003. *Phys. Rev.,* 67**,** 224303.

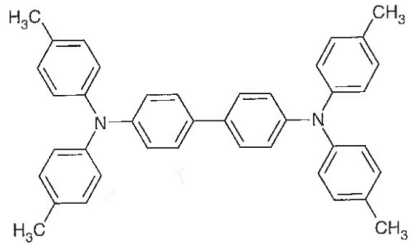
Poole-Frenkel Effect

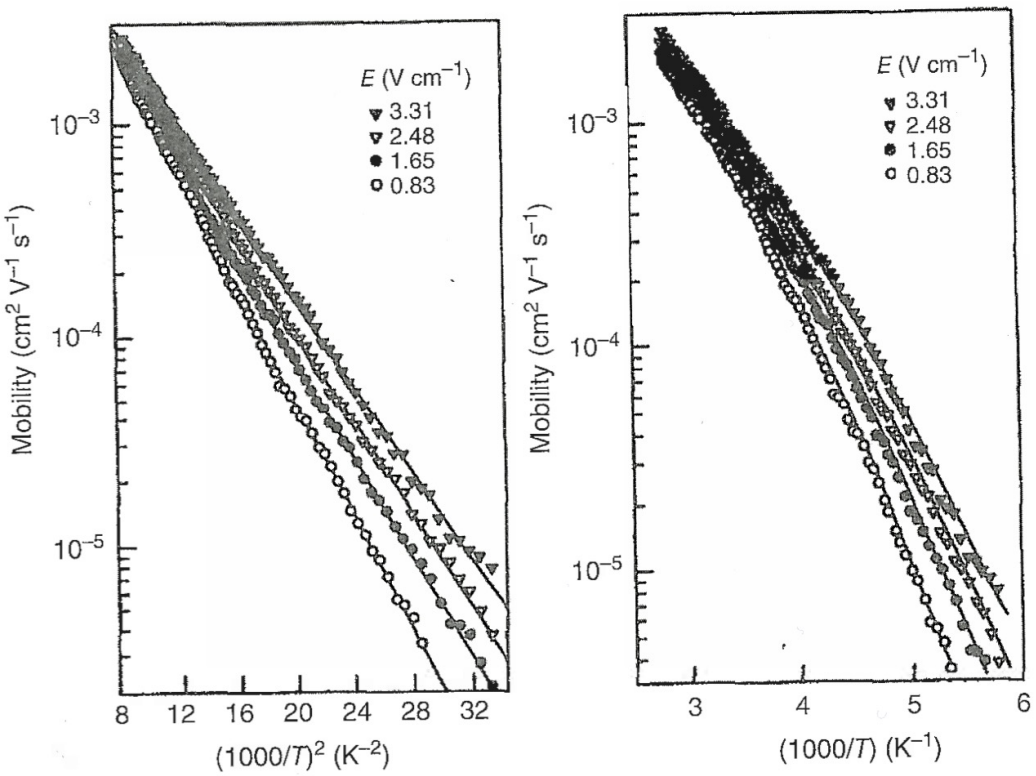
- Trap barrier lowering due to external field

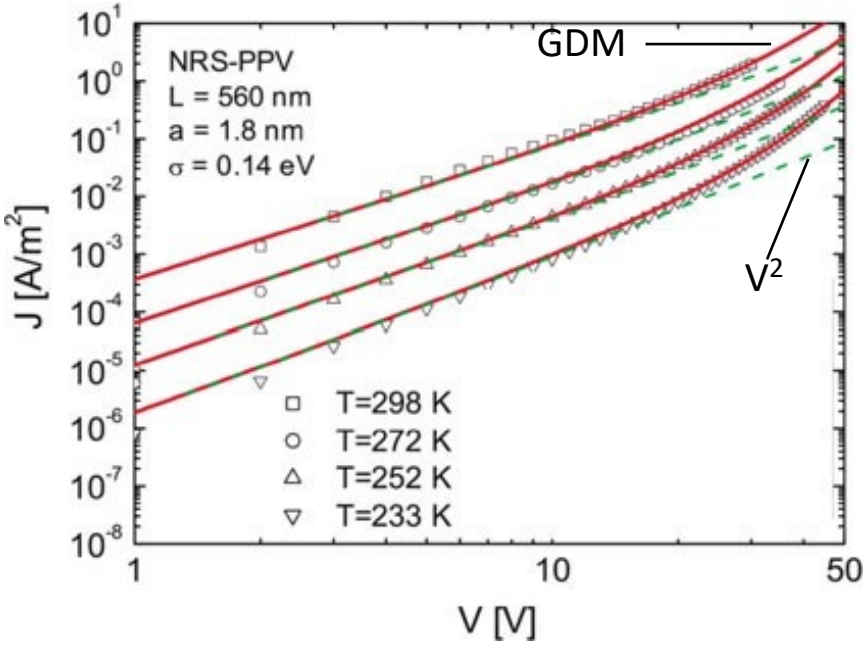


$$\mu \sim \exp\left(\beta\sqrt{F}\right)$$

Tests of mobility theory







Pasveer, W. F. et al, 2005. *Phys. Rev. Lett.,* 94**,** 206601.

$1/T^2$ & $F^{1/2}$ dependence

Current and Conductivity

1. **Ohm's Law** (gives DC mobility).

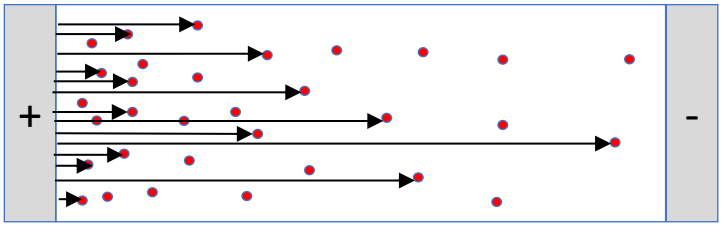
- For a single carrier (holes in this case) in a uniform electric field:

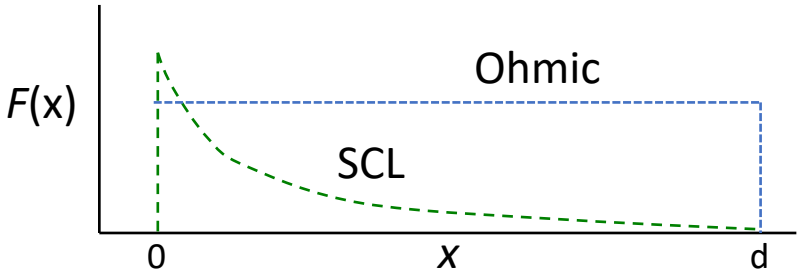
$$j = qp\mu F = qp\mu \frac{V}{d}$$

- Gives the product $p\mu \Rightarrow$ requires independent determination of charge density.
- *Ohmic regime* identified by *linear* relationship between *j* and *V.*

2. **Space charge limited current** (gives DC mobility).

- When the injected carrier density $p_{inj} > p_0$ (the background charge density), charge accumulates at electrodes:





Similar to Monte Carlo Expressions

Widely used expressions for mobility in disordered systems based on Miller-Abrahams:
(fits transient characteristics as well)

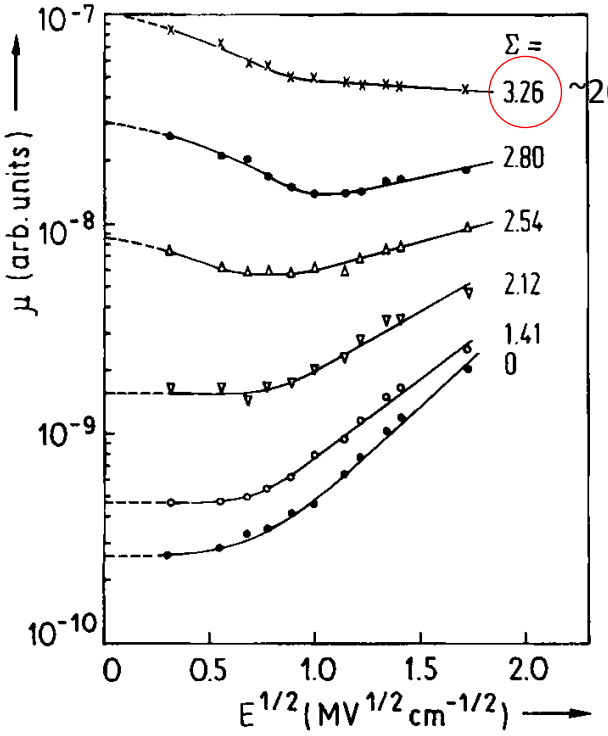
$$\mu(\hat{\sigma},\Sigma,F)=\mu_0\exp\left(-\left(\tfrac{2}{3}\hat{\sigma}\right)^2\right)\begin{cases}\exp C\left(\hat{\sigma}^2-\Sigma^2\right)\sqrt{F} & \Sigma\geq 1.5\\ \exp C\left(\hat{\sigma}^2-2.25\right)\sqrt{F} & \Sigma<1.5\end{cases}$$

$$\mu_0\sim\frac{J^2}{F^2}$$

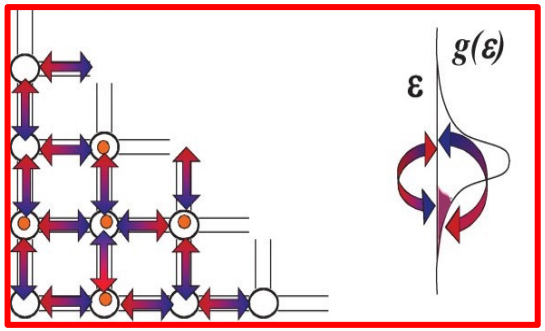
Positional disorder parameter

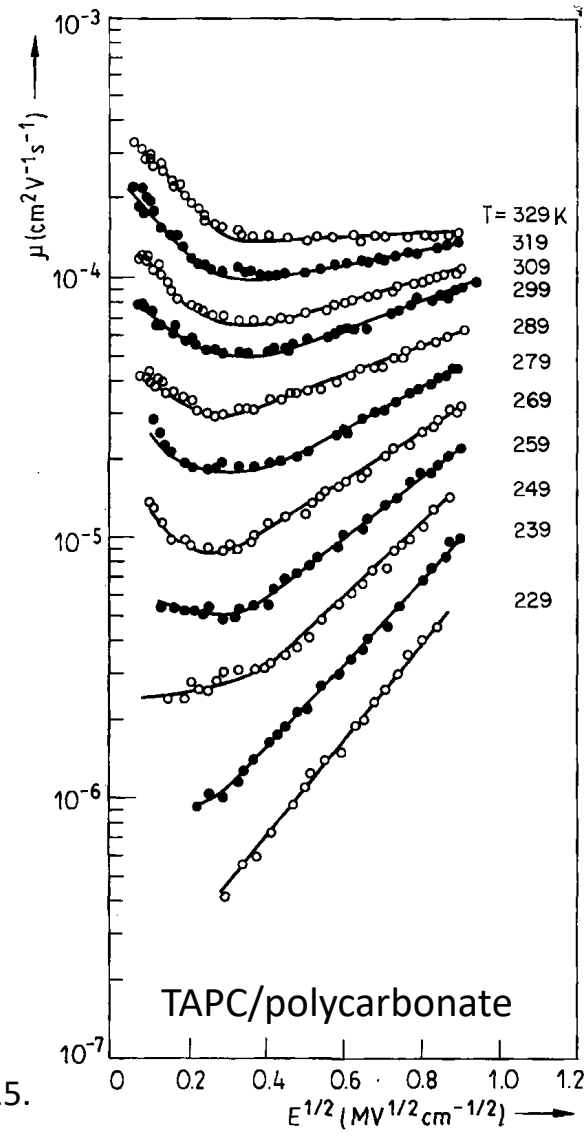
$$\hat{\sigma}=\frac{\sigma}{k_BT}$$

Energetic disorder parameter C=3x10^{-4} cm^{½}V$^{-½}$



~20% disorder





Bässler, H. 1993. *Phys. Stat. Sol.*, 175, 15.

Space Charge Limited Current

- In the space charge regime, we make the following assumptions to solve *j* vs. *V* :
  - $p_{inj} > p_0$
  - Only one carrier type is present
  - $\mu \neq \mu(F)$ (Field-independent mobility)
  - Free carrier distribution follows Boltzmann statistics
  - Trapped charge occupation defined by Fermi statistics
  - *F* is large enough for drift (and not diffusion) to dominate
  - Field not so large that field emission is important

- In 1D, Gauss says: $\frac{dF}{dx} = \frac{q\left(p_{inj}(x) + p_t(x) + p_0\right)}{\varepsilon} \approx \frac{qp_{inj}(x)}{\varepsilon}$ (trap free case)
  - $\varepsilon = \varepsilon_0 \varepsilon_r$
  - Current in the absence of trapped charge, p_t(x): $j(x) = q\mu_p p_{inj}(x) F(x)$
  - Now: $\frac{dF^2(x)}{dx} = 2F(x)\frac{dF(x)}{dx} = \frac{2qp_{inj}(x)F(x)}{\varepsilon} = \frac{2j(x)}{\varepsilon\mu_p}$
  - Since *j* is constant across layer $\Rightarrow F^2(x) = \frac{2jx}{\varepsilon\mu_p}$ (This is current continuity)

j-V in the SCL regime

$$F^2(x) = \frac{2jx}{\varepsilon\mu_p} \Rightarrow F(x) = \sqrt{\frac{2jx}{\varepsilon\mu_p}}$$

Note: $F(x) \sim x^{1/2}$ vs. $F(x)$= constant for Ohmic

Now potential is: $-\frac{dV}{dx} = F(x)$

Integrating between $0 < V < V_a$ and $0 < x < d$

We obtain: $V_a = \frac{2}{3}\sqrt{\frac{2jd^3}{\varepsilon\mu_p}}$

Giving the **Mott-Gurney relationship**:

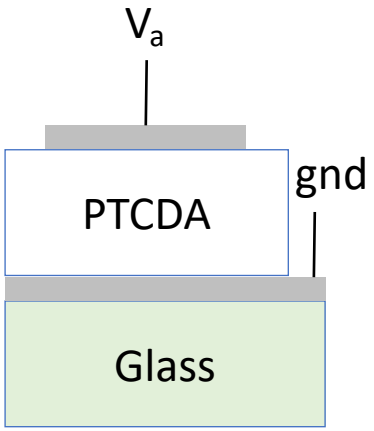
$$j = \frac{9}{8}\mu_p\varepsilon\frac{V_a^2}{d^3}$$

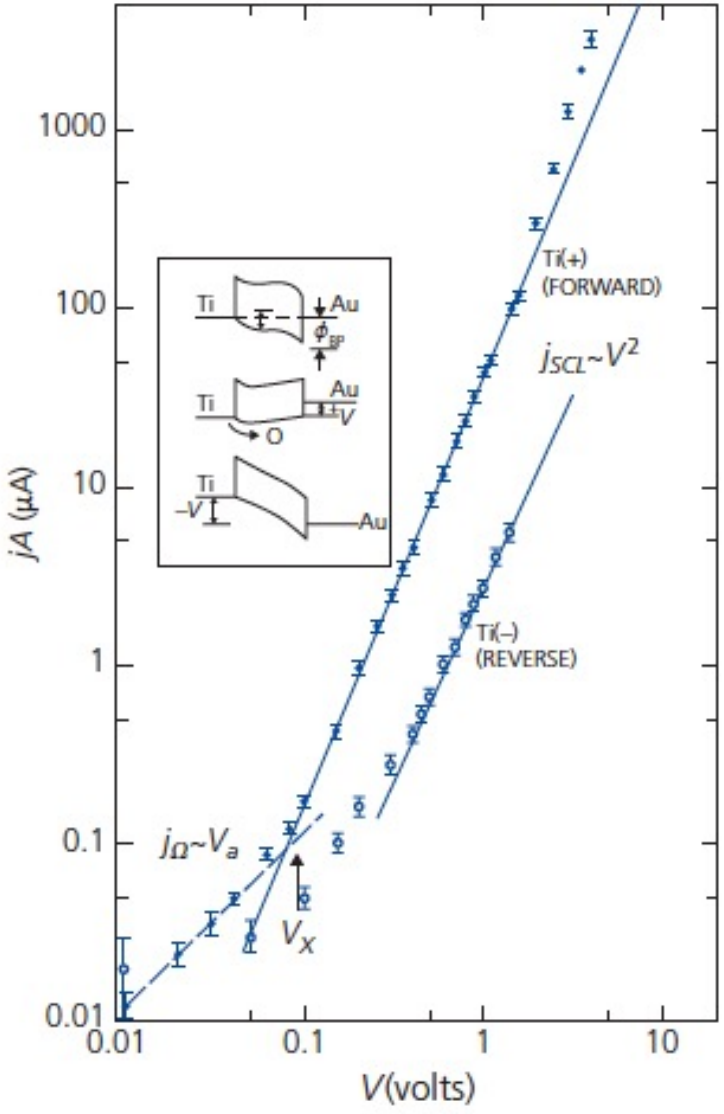
Note the absence of *p*!

⇒ Only need the dielectric constant and the film thickness.

Use the ohmic region of the *j-V* curve to determine p_0.

SCL Current in PTCDA





To find background carrier density:

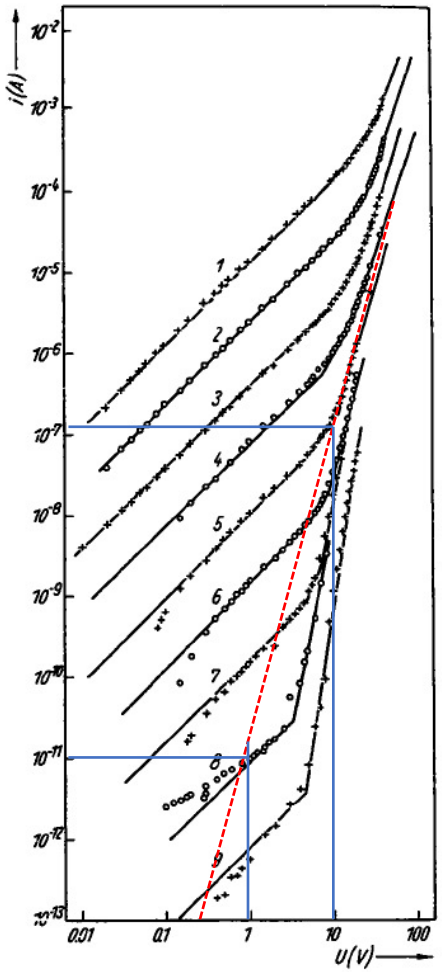
At V_x: j(ohmic)=j(SCL)

$$\Rightarrow qn\mu\frac{V_x}{d}=\frac{9}{8}\mu\varepsilon\frac{V_x^2}{d^3}$$

$$\Rightarrow n=\frac{9}{8}\frac{\varepsilon}{q}\frac{V_x}{d^2}$$

Forrest, S. R., Kaplan, M. L. & Schmidt, P. H. 1984 *J. Appl. Phys.,* 55**,** 1492.

The truth is in the data



$j \sim V^4$

This isn't simple SCL current,
in which case $j \sim V^2$

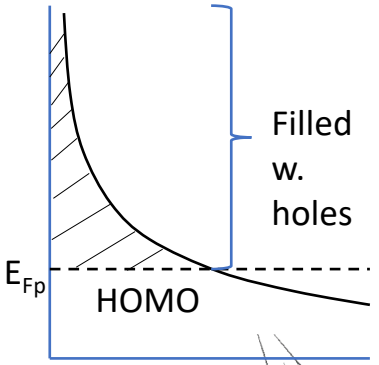
This is SCL in the presence of a high density of traps

Let the data speak to you, not vice versa

But what happens if things aren't so simple?

- We have assumed no traps. In organics, this is not often the case due to ***static disorder*** (i.e. defects in the solid, stacking faults).
- Simplest case: A single discrete, shallow trap where $\frac{p_0}{p_t} = \Theta << 1$
- Then <u>you</u> can show: $j = \frac{9}{8}(\Theta\mu_p)\varepsilon\frac{V_a^2}{d^3}$
  - ➢ That is, the mobility is now reduced by Θ
- More often there is an exponential distribution of traps, in which case we have trap-filled limited conduction:

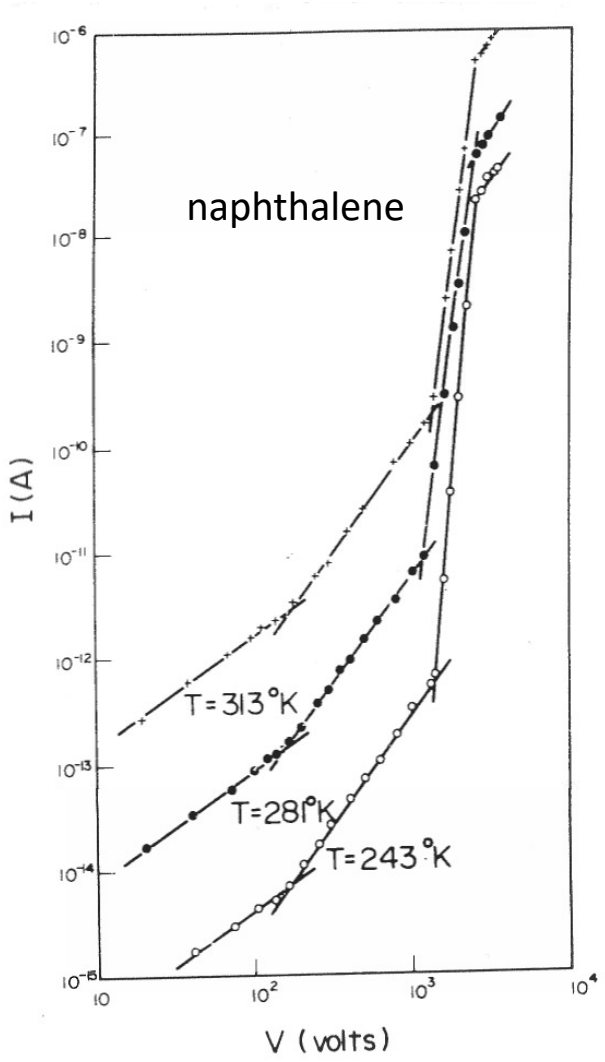
$$j_{TFL} = q\mu N_{HOMO}\left[\frac{\varepsilon m}{q(m+1)N_t}\right]^m\left[\frac{2m+1}{m+1}\right]^{m+1}\frac{V_a^{m+1}}{d^{2m+1}}$$

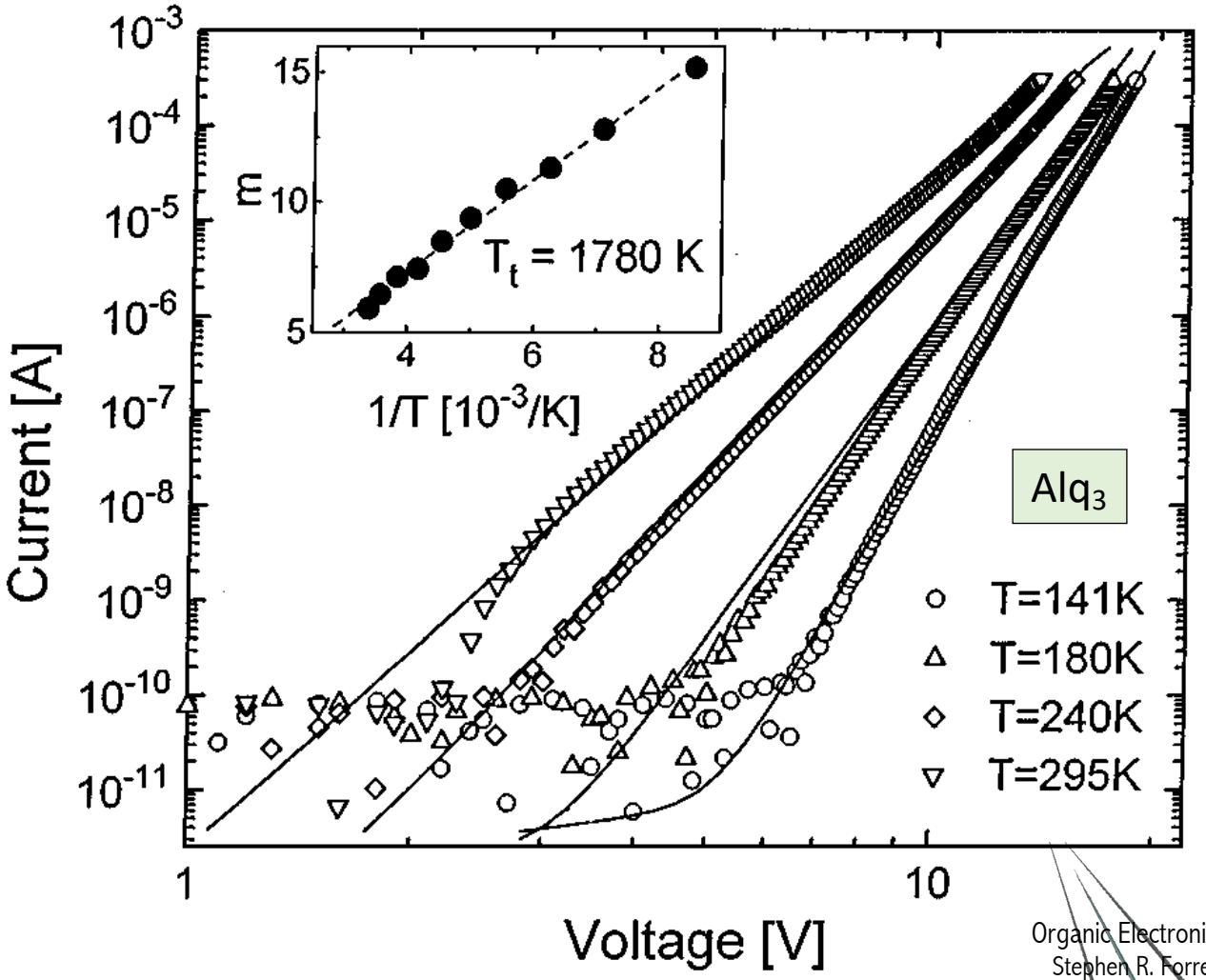


- $m=T_t/T$ where T_t is the characteristic trap temperature
  - Define $p_t = N_t\exp\left(-\left(E_{Fp}-E_{HOMO}\right)/k_BT_t\right)$
  - Leading to: $p = N_{HOMO}\exp\left(-\left(E_{Fp}-E_{HOMO}\right)/k_BT\right) = N_{HOMO}\exp\left(-\left(E_{Fp}-E_{HOMO}\right)/k_BT_t\left[T_t/T\right]\right)$

$$p = N_{HOMO}\left(\frac{p_t}{N_t}\right)^{T_t/T} \Rightarrow p_t = N_t\left(\frac{p}{N_{HOMO}}\right)^{1/m}$$

Examples of TFL-SCL





Multiple ohmic, SCL and TFL regions

M. Campos, Mol. Cryst. Liq. Cryst. **18**, 105 (1972)

P. E. Burrows, et al., *J. Appl. Phys.*, **79**, 7991 (1996).