The Fundamentals of Organic Thermoelectic Materials

Martijn Kemerink
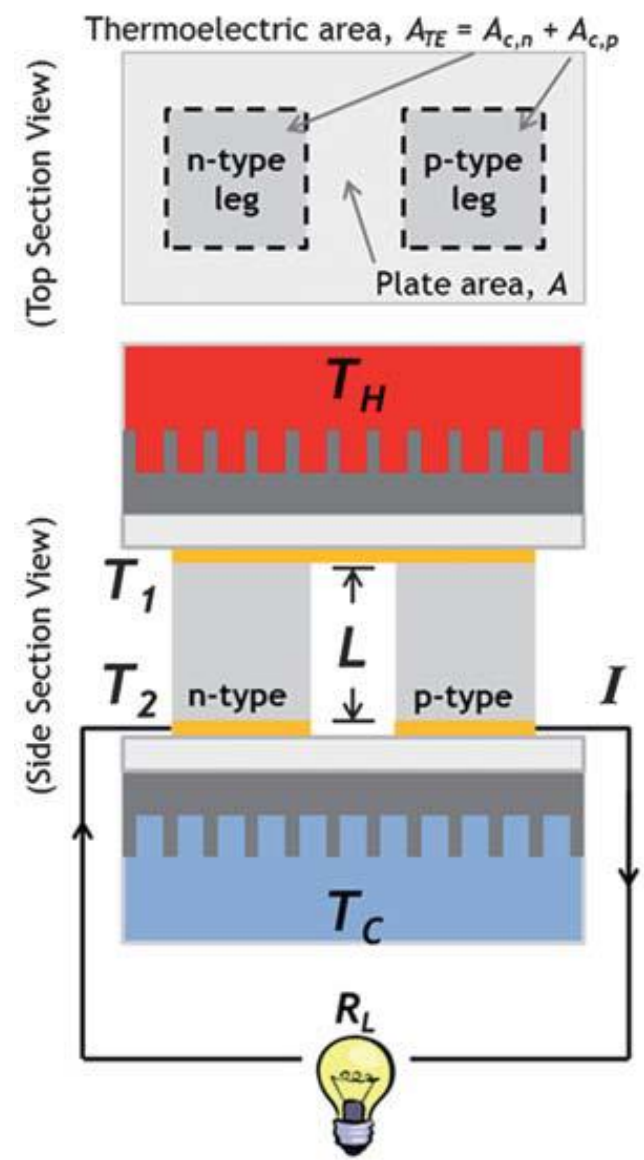
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Outline

- Introduction: metrics for (organic) thermoelectrics
  - ZT
  - $/Watt

- Fundamentals of charge and energy transport
  - Boltzmann transport equations
  - metallic systems

- Charge transport in organic semiconductors
  - energetic disorder
  - mobility edge model
  - hopping models & percolation
    - constant DOS
    - Gaussian disorder model (GDM)

- Beyond GDM
  - transport edge model
  - DOS design
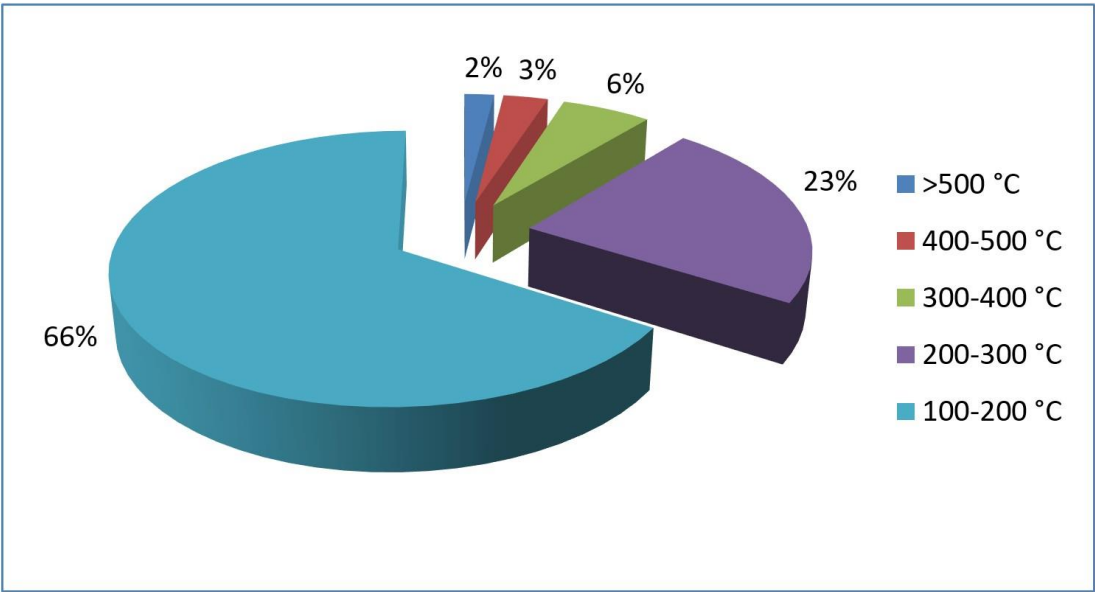   - role of dopant ions
    - semiconductor blends

quiz…

Thermoelectric area, $A_{TE} = A_{c,n} + A_{c,p}$

(Top Section View)

n-type leg   p-type leg

Plate area, A

(Side Section View)

T_H

T_1

T_2 n-type L p-type I

T_C

R_L

(low) quality of waste heat

2% 3% 6%

23%

66%

- >500 °C
- 400-500 °C
- 300-400 °C
- 200-300 °C
- 100-200 °C

http://www.interreg-central.eu / 28 06 2017

$$\eta = f(ZT)\eta_{Carnot} = f(ZT)\frac{T_h - T_c}{T_h}$$

Yee et al., *En. Environ. Sci.* **2013**, *6*, 2516

Metric 1: ZT

$$\text{ZT} = \frac{\sigma S^2}{\kappa}T = \frac{\text{PF}}{\kappa}T$$

σ - electrical conductivity
κ - thermal conductivity
S – Seebeck coefficient
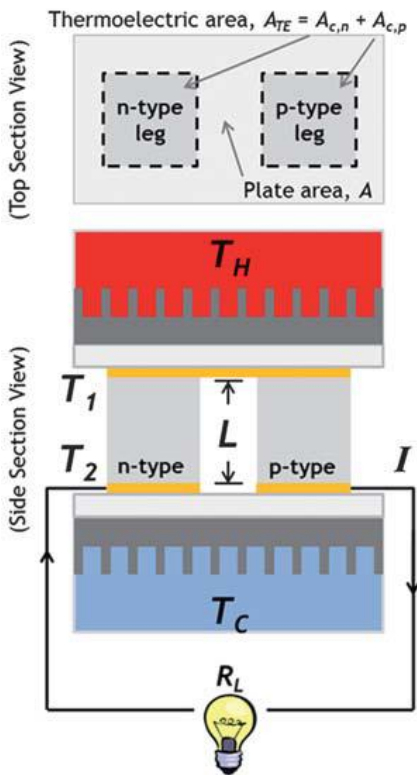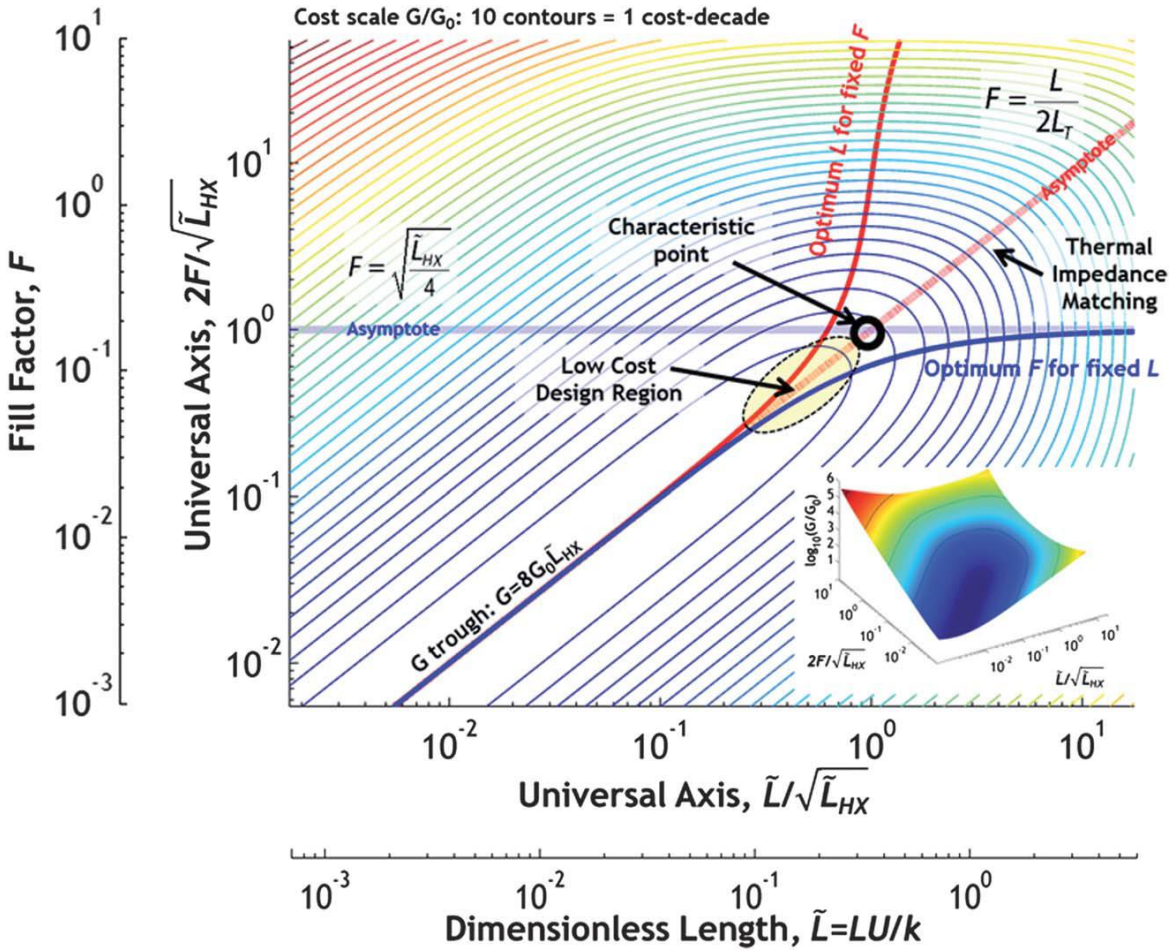
Metric 2: module $ per W: *G*

Metric 1: ZT

$$ZT = \frac{\sigma S^2}{\kappa} T = \frac{PF}{\kappa} T$$

σ - electrical conductivity
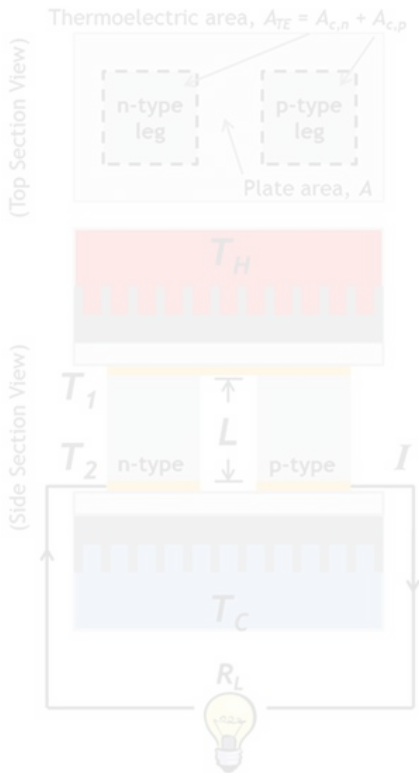κ - thermal conductivity
S – Seebeck coefficient

Thermoelectric area, $A_{TE} = A_{c,n} + A_{c,p}$

(Top Section View)

n-type leg   p-type leg

Plate area, A

(Side Section View)

T_H

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T_2 n-type L p-type I
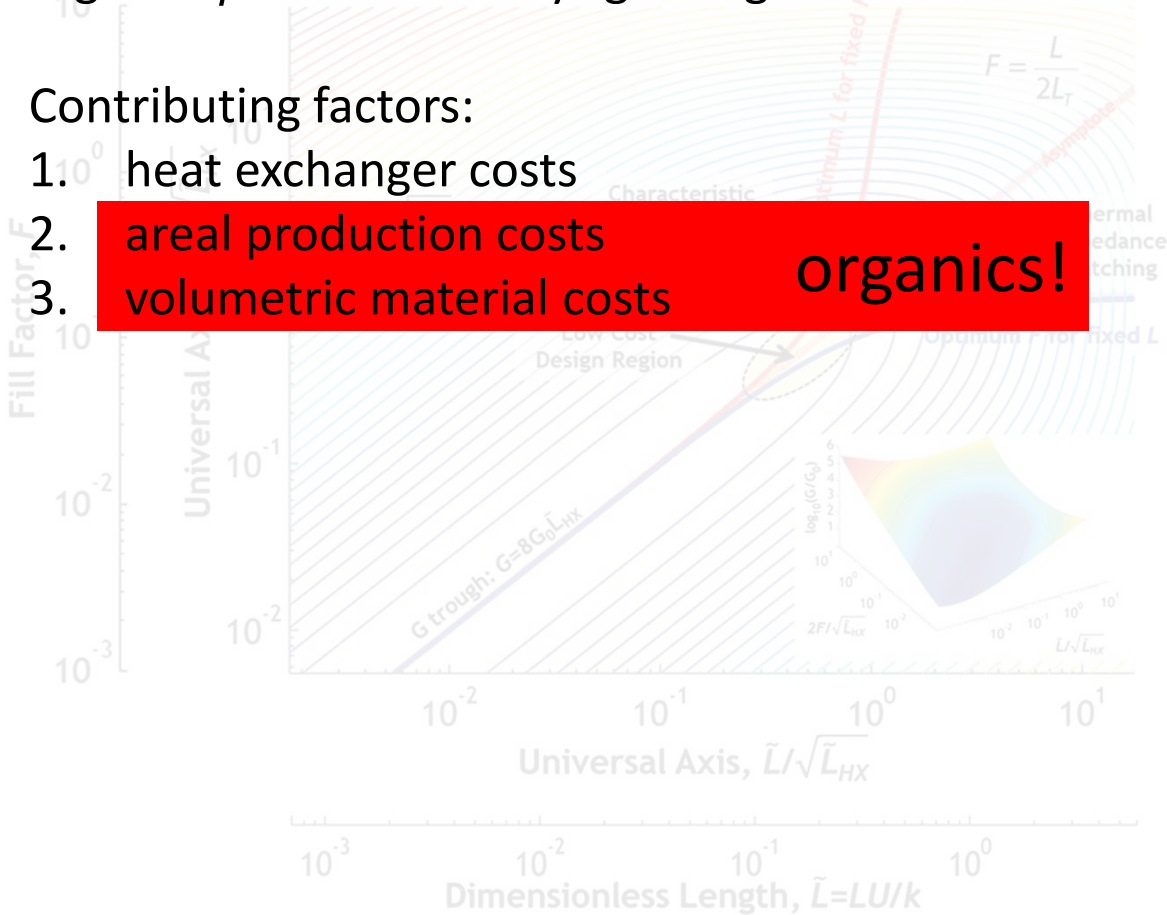
T_C

R_L

Metric 2: module $ per W: *G*

Highest η does not always give highest G!

Contributing factors:
1. heat exchanger costs
2. areal production costs
3. volumetric material costs

organics!

$F = \frac{L}{2L_T}$

Characteristic

Low Cost
Design Region

G trough: $G=8G_0\tilde{L}_{HX}$

Fill Factor

Universal Axis

10^0

10^{-1}

10^{-2}

10^{-3}

Universal Axis, $\tilde{L}/\sqrt{\tilde{L}_{HX}}$

10^{-2} 10^{-1} 10^0 10^1

10^{-3} 10^{-2} 10^{-1} 10^0

Dimensionless Length, $\tilde{L}=LU/k$

Metric 2: $ per W: G

Contributing factors:
1. heat exchanger costs
2. areal production costs
3. volumetric material costs

To Do…

1. get rid of the heat exchanger…
2. design TEG for optimal G, not P or η
3. optimize ZT
   → **increase σ and/or S**

$$\text{ZT} = \frac{\sigma S^2}{\kappa}T = \frac{\text{PF}}{\kappa}T$$

Current status

all numbers are approximate	σ (S/cm)	κ (W/m/K)	S (μV/K)	ZT @ RT (-)
Bi_2Te_3	682	1.57	464	1
organics (p-type)	100	0.37	200	0.25
organics (n-type)	3.1	0.25	-568	0.11

Organics are not rare or toxic!

Huang et al., *JACS* **2017**, *139*, 13013
Bubnova et al., *Nat. Mater.* **2011**, *10*, 429
Yee et al., *En. Environ. Sci.* **2013**, *6*, 2516

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  - ZT
  - $/Watt

- **Fundamentals of charge and energy transport**
  - **Boltzmann transport equations**
  - **metallic systems**

- Charge transport in organic semiconductors
  - energetic disorder
  - mobility edge model
  - hopping models & percolation
    - constant DOS
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- Beyond GDM
  - transport edge model
  - DOS design
    - role of dopant ions
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In general, transport involving irreversible processes can be described by the phenomenological transport relations. For $n = 2$:

$$J_1 = L_{11}X_1 + L_{12}X_2$$
$$J_2 = L_{21}X_1 + L_{22}X_2$$

J_i: generalized fluxes
X_j: generalized forces
L_{ij}: generalized conductances

with

$$L_{12} = L_{21}$$

reciprocity relation

The reciprocity relation was formally derived by Onsager (1931) on basis of microscopic reversibility. Hence, it holds as long as $B = 0$.

Transport equations

For the case of combined charge and heat transport, the phenomenological equations become:

$$j = L_{11}\varepsilon + L_{12}(-\nabla T)$$ electrical current density

$$j^q = L_{21}\varepsilon + L_{22}(-\nabla T)$$ heat current density

with

$$L_{12} = L_{21}/T$$ reciprocity relation

and

$$\varepsilon = E + \frac{\nabla \mu}{q}$$

E: electric field
μ: chemical potential

For the case of combined charge and heat transport, the phenomenological equations become:

$$j = L_{11}\varepsilon + L_{12}(-\nabla T)$$ electrical current density
$$j^q = L_{21}\varepsilon + L_{22}(-\nabla T)$$ heat current density

Electrical conductivity: constant T, apply E, measure j, compare to $j = \sigma E$

$$L_{11} = \sigma$$

Thermal conductivity: isolate electrically ($j = 0$), apply ∇T, measure heat flux j^q

$$j = 0 \rightarrow \varepsilon = \frac{L_{12}}{L_{11}} \nabla T \quad \text{and hence} \quad j^q = \left(L_{22} - L_{21} \frac{L_{12}}{L_{11}} \right)(-\nabla T)$$

comparison to the Poisson law $j^q = -\kappa \nabla T$ gives

$$\kappa = L_{22} - L_{21} \frac{L_{12}}{L_{11}} \quad \text{(and NOT just } \kappa = L_{22}\text{)}$$

To stop the current flow carried by the flux of heat, and electric field has to build up ($j = 0$, $\varepsilon \neq 0$) → thermopower…

See e.g. Ziman, 'Electrons and Phonons: The Theory of Transport Phenomena in Solids'

For the case of combined charge and heat transport, the phenomenological equations become:

$$j = L_{11}\varepsilon + L_{12}(-\nabla T)$$ electrical current density

$$j^q = L_{21}\varepsilon + L_{22}(-\nabla T)$$ heat current density

Thermopower: apply ∇T, enforce $j = 0$, measure E, compare to $\Delta V = -S\Delta T$

$$j = 0 \rightarrow \varepsilon = \frac{L_{12}}{L_{11}}\nabla T \quad \text{and hence} \quad S = \frac{L_{12}}{L_{11}}$$

In practice the absolute thermopower is difficult to measure due to the unavoidable temperature difference over the measurement apparatus.
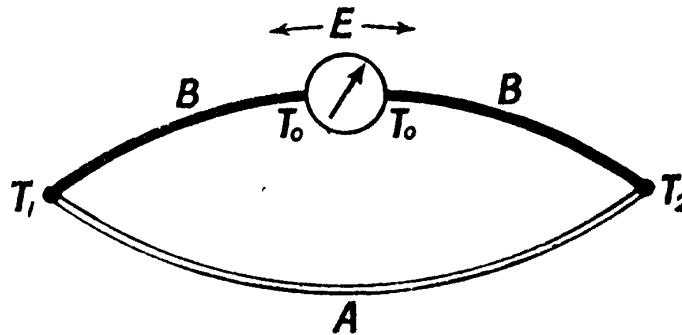
FIG. 81. Measurement of Seebeck effect.

See e.g. Ziman, 'Electrons and Phonons: The Theory of Transport Phenomena in Solids'

For the case of combined charge and heat transport, the phenomenological equations become:

$$j = L_{11}\varepsilon + L_{12}(-\nabla T)$$ electrical current density
$$j^q = L_{21}\varepsilon + L_{22}(-\nabla T)$$ heat current density

Peltier effect: recall conductivity measurement ($\nabla T = 0$), then

$$\varepsilon = \frac{j}{L_{11}}$$ and hence $$j^q = \frac{L_{21}}{L_{11}}j$$

Hence, the electrical current is accompanied by a heat current. Comparing to $j^q = \Pi j$ gives

$$\Pi = \frac{L_{21}}{L_{11}}$$

and using $S = \frac{L_{12}}{L_{11}}$ and the reciprocity relation $L_{12} = L_{21}/T$ we get the

Kelvin relation:
$$\Pi = TS$$

See e.g. Ziman, 'Electrons and Phonons: The Theory of Transport Phenomena in Solids'

For the case of combined charge and heat transport, the phenomenological equations become:

$$j = L_{11}\varepsilon + L_{12}(-\nabla T)$$ electrical current density
$$j^q = L_{21}\varepsilon + L_{22}(-\nabla T)$$ heat current density

Electrical conductivity: $\sigma = L_{11}$

Thermal conductivity:
(electronic contribution only!)

$$\kappa = L_{22} - L_{21}\frac{L_{12}}{L_{11}} = \kappa'\left(1 - \frac{S^2\sigma T}{\kappa'}\right)$$

$$= \kappa'(1 - ZT)$$

Thermopower: $$S = \frac{L_{12}}{L_{11}}$$

Peltier effect: $$\Pi = \frac{L_{21}}{L_{11}}$$

small in metals, not small in thermoelectric materials!

Kelvin relation: $$\Pi = TS$$

See e.g. Ziman, 'Electrons and Phonons: The Theory of Transport Phenomena in Solids'

To be useful, the coefficients L_{ij} in the transport equations,
$j = L_{11}\varepsilon + L_{12}(-\nabla T)$ and
$j^q = L_{21}\varepsilon + L_{22}(-\nabla T)$,
should be calculable. For metallic systems, an established way of doing this is by Boltzmann transport theory. In the relaxation time approximation, this gives:

$$L_{11} = \mathcal{L}^{(0)}$$
$$L_{21} = TL_{12} = -\frac{1}{q}\mathcal{L}^{(1)}$$
$$L_{22} = \frac{1}{q^2 T}\mathcal{L}^{(2)}$$

with

$$\mathcal{L}^{(\alpha)} = \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon - \varepsilon_F)^\alpha \sigma(\varepsilon)$$

and

$$\sigma(\varepsilon) = q^2 \tau(\varepsilon) \int \frac{d\boldsymbol{k}}{4\pi^3}\delta\big(\varepsilon - \varepsilon(\boldsymbol{k})\big)\boldsymbol{v}(\boldsymbol{k})\boldsymbol{v}(\boldsymbol{k})$$

See e.g. Ashcroft & Mermin, 'Solid State Physics', International Edition, 1976
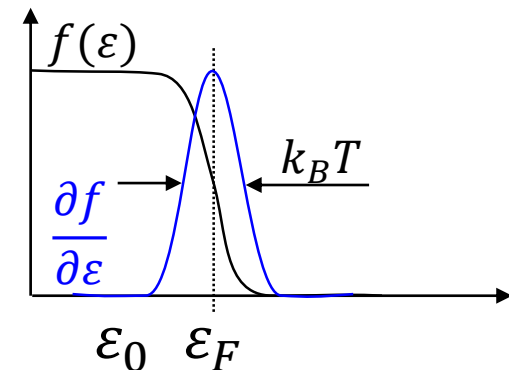
- f is the Fermi-Dirac distribution function; $f(\varepsilon) = 1/(1 + \exp((\varepsilon - \varepsilon_F)/k_B T))$

- In $\mathcal{L}^{(\alpha)} = \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon - \varepsilon_F)^\alpha \sigma(\varepsilon)$ the term $\sigma(\varepsilon)$ is the conductivity distribution function such that

$$\sigma = \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon}\right) \sigma(\varepsilon)$$

  While $\sigma(\varepsilon)$ may be associated with the conductivity a metal would show if its Fermi energy were equal to ε, it cannot be measured!

- Once we know $\sigma(\varepsilon)$, all thermoelectric properties can be calculated! σ, S, Π and κ cannot be changed independently.

- In the following we shall be concerned with determining (approximations for) $\sigma(\varepsilon)$ for various systems. For convenience, the derivative of f shall often be integrated in $\sigma(\varepsilon)$.
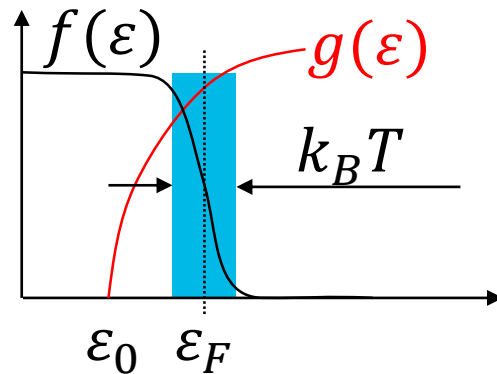
See e.g. Ashcroft & Mermin, 'Solid State Physics', International Edition, 1976

For metallic systems ($kT \ll \varepsilon_F$) …

… one can use the Sommerfeld expansion of $\mathcal{L}^{(\alpha)}$ and obtain

$$\mathrm{L}_{11} = \sigma(\varepsilon_F) = \sigma$$

$$L_{21} = T L_{12} = -\frac{\pi^2}{3q}(k_B T)^2 \sigma' \quad \text{with } \sigma' = \frac{\partial}{\partial \varepsilon}\sigma(\varepsilon)\Big|_{\varepsilon_F}$$

$$L_{22} = \frac{\pi^2}{3}\left(\frac{k_B}{q}\right)^2 T\sigma = \kappa'$$

- Since for a metallic system $ZT \ll 1$ we have

$$\kappa = \kappa'(1 - ZT) \approx \kappa' = \frac{\pi^2}{3}\left(\frac{k_B}{q}\right)^2 T\sigma = L_0\left(\frac{k_B}{q}\right)^2 T\sigma$$

which is the Wiedemann-Franz law.

Wiedemann-Franz law in highly doped organics?

The Wiedemann-Franz law as derived for metallic conduction:

$$\kappa_{el} = \frac{\pi^2}{3}\left(\frac{k_B}{q}\right)^2 T\sigma = L_0\left(\frac{k_B}{q}\right)^2 T\sigma$$

with L_0 the Lorentz factor.
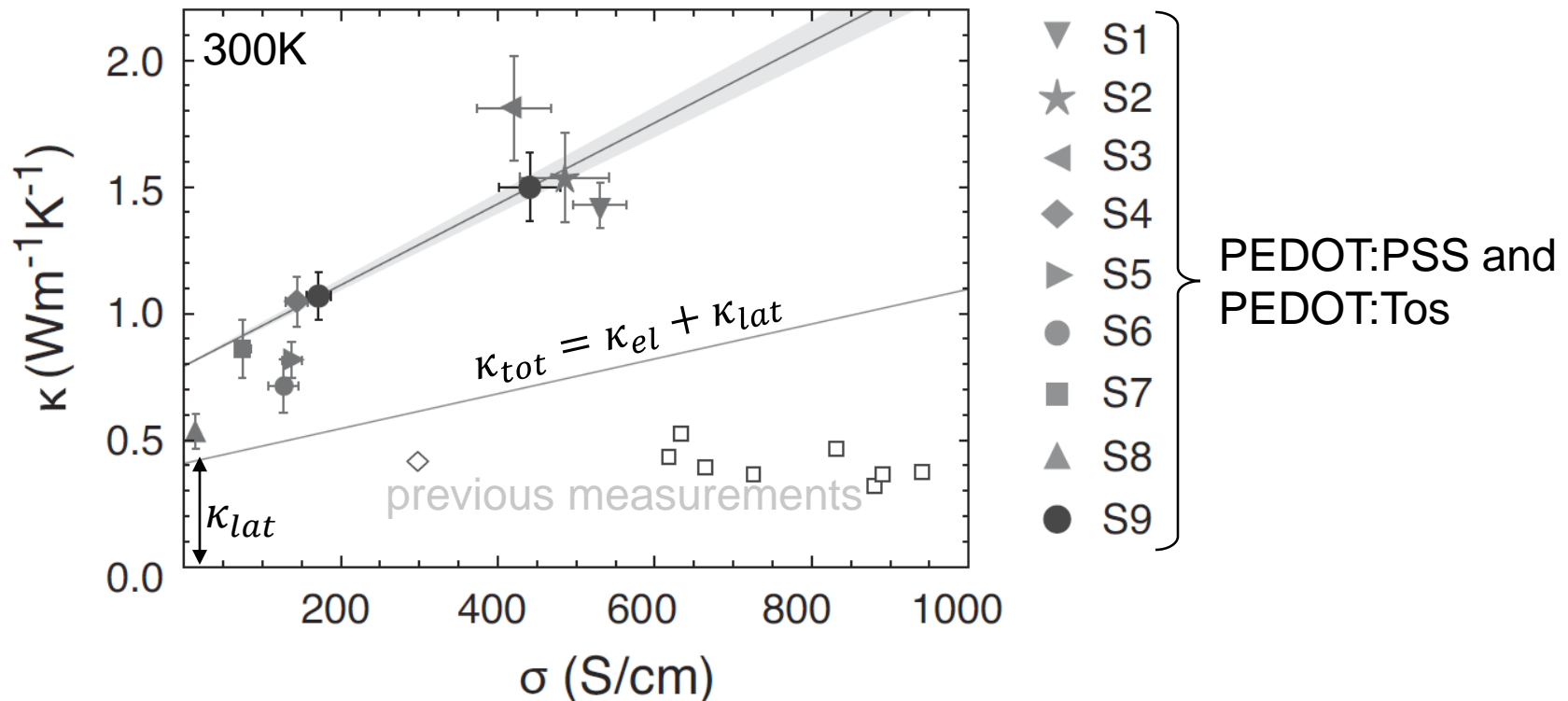
- The lattice contribution κ_{lat} must be added to the electronic contribution from WF
- The fitted value for L exceeds L_0 by $\sim 2.3 \times$
- More work needed!
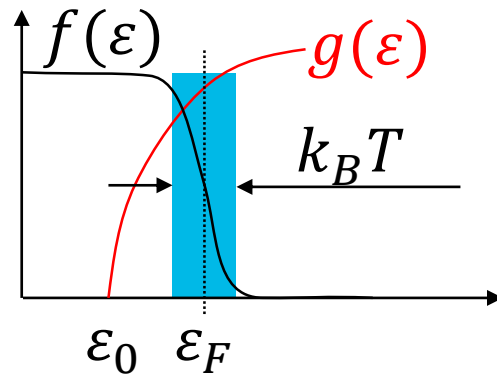
Weathers et al., *Adv. Mater.* **2015**, *27*, 2101-2106

For metallic systems ($kT \ll \varepsilon_F$) …

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$$L_{22} = \frac{\pi^2}{3}\left(\frac{k_B}{q}\right)^2 T\sigma = \kappa'$$

- $S = \dfrac{L_{12}}{L_{11}} = -\dfrac{\pi^2}{3q}k_B^2 T\dfrac{\sigma'}{\sigma} = -\dfrac{\pi^2}{3q}k_B^2 T\dfrac{d(\ln\sigma(\varepsilon))}{d\varepsilon}\Big|_{\varepsilon_F}$

  which is sometimes called the Mott expression for S. It does not generally hold for hopping systems!

Ashcroft & Mermin, 'Solid State Physics', International Edition, 1976
Mott & Davis, 'Electronic Processes in Non-Crystalline Materials', 2nd Edition, 1979
S. Ihnatsenka et al., *Phys. Rev. B.* **92**, 035201 (2015)

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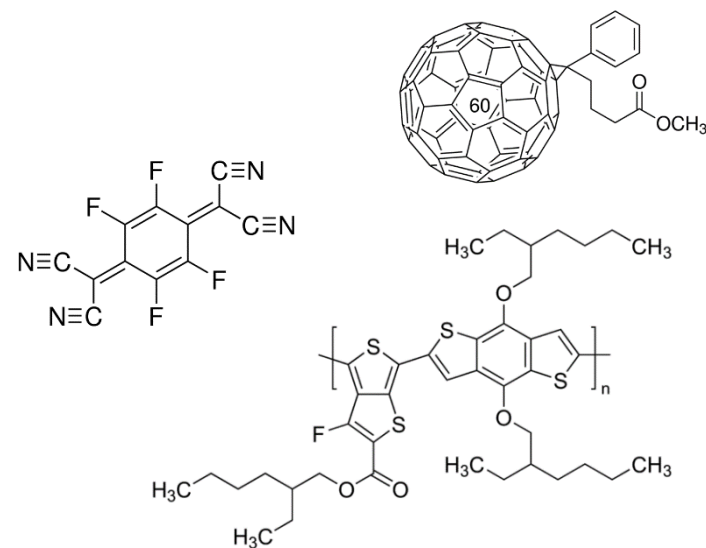
Delocalization of charge carriers limited by defects and therefore limited to a chain segment.

Conformational defect e.g. twisting of rings

Chemical defect

Chain segment

Chain end
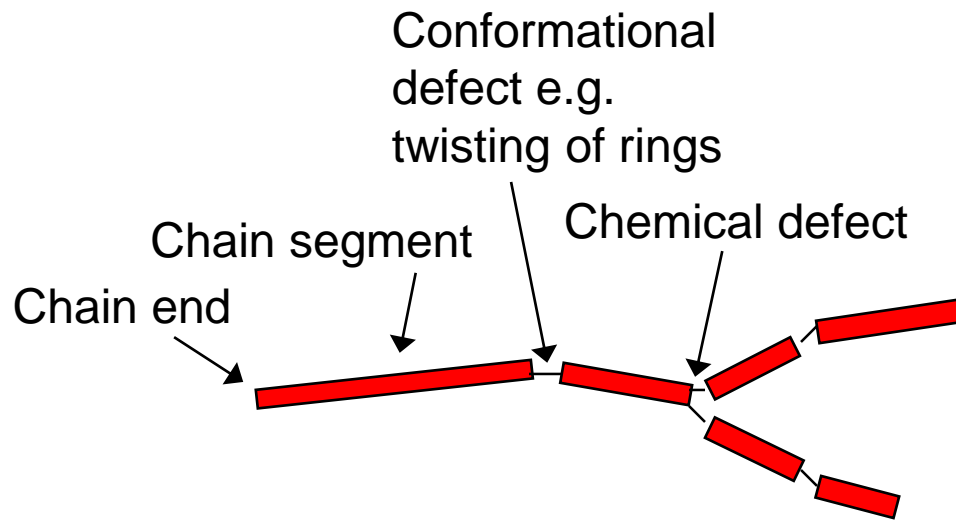
Defects occur randomly, giving rise to a distribution for the delocalization length of the carriers ($\propto$ segment size). The energy of the carrier depends on the degree of delocalization so there is a broad distribution of energy levels associated with the segments.

Apart from confinement effects also differences in local morphology, polarizability and the presence of charged species (mono-, di- & quadrupoles) can give rise to *static energetic disorder*. There exists also dynamic disorder that will not be discussed here.

conformational defect e.g. twisting of rings

aggregated region

amorphous region

chain segment

chemical defect

chain end

charged species
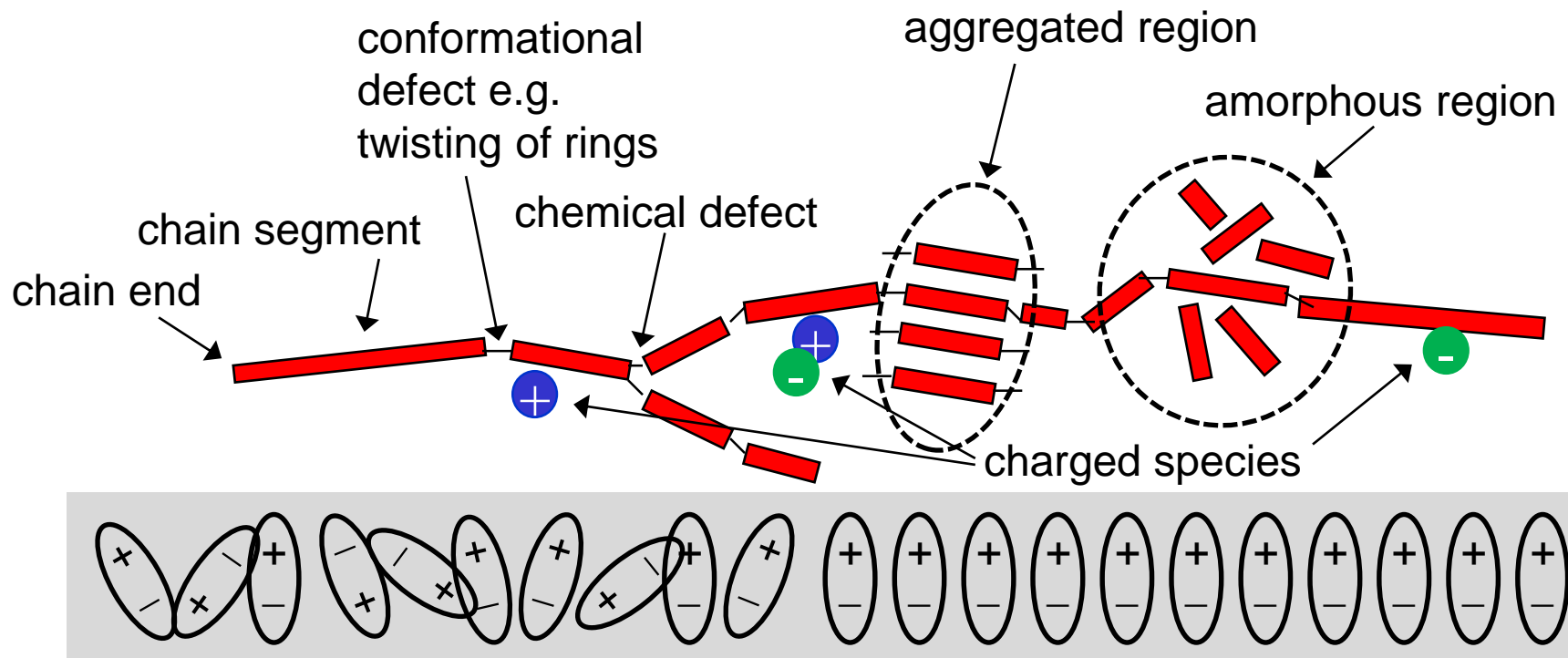
on OFET: substrate with dipolar (dis)order

There are many and strong indications that the disorder in OFETs is different than in e.g. OLEDs due to the substrate.
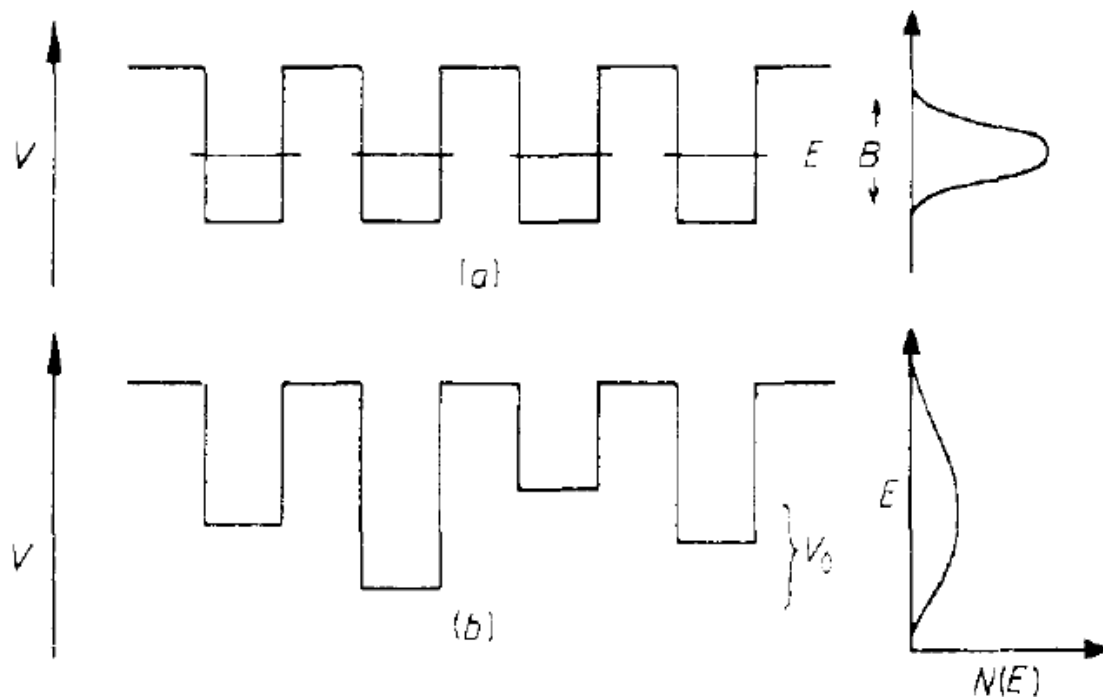
$V_0 = 0 \rightarrow$ Bloch waves:

$$\Psi = \sum_n \exp(ika_n)\psi(r - a_n)$$

$$B = 2zI$$

with:

B: bandwidth

z: coordination nr. of lattice

I: transfer integral

V_0: magnitude of disorder potential

Figure 2. Potential energy function introduced by Anderson (1958). (a), In the absence of a random potential; (b), with random potential. The density of states is also shown.

N. Mott, J. Phys. C: Solid State Phys. **20**, 3075 (1987).
P.W. Anderson, Phys. Rev. **109**, 1492 (1958).

In case the disorder is sufficiently large* there exists a well defined energy above (below) which all states are extended (localized). This is the '*Mobility Edge*'.

mobility edge E_C

density of states $N(E)$

energy E

E_A E_c

localized states   extended states
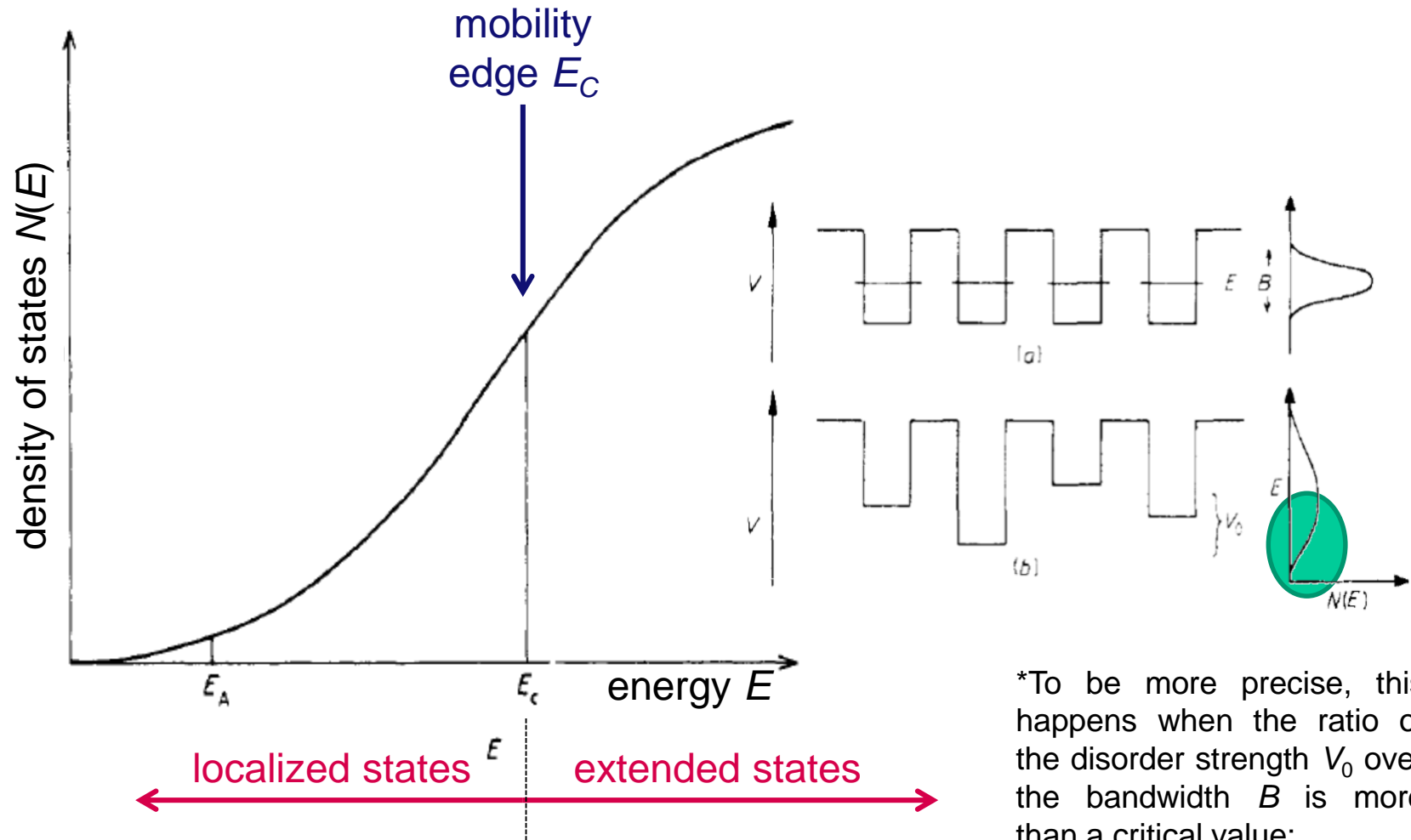
*To be more precise, this happens when the ratio of the disorder strength V_0 over the bandwidth B is more than a critical value:

$$V_0/B > 1.6$$

for 3D with coordination number 6 (cubic lattice)

N.F. Mott, J. Phys. C: Solid State Phys. **20**, 3075 (1987).

Disorder – Mobility Edge model

Assumption: only delocalized states contribute to the charge transport.

mobility edge E_C

Fermi energy E_F

density of states $N(E)$

E_A

E_c

energy E

E

localized states   extended states
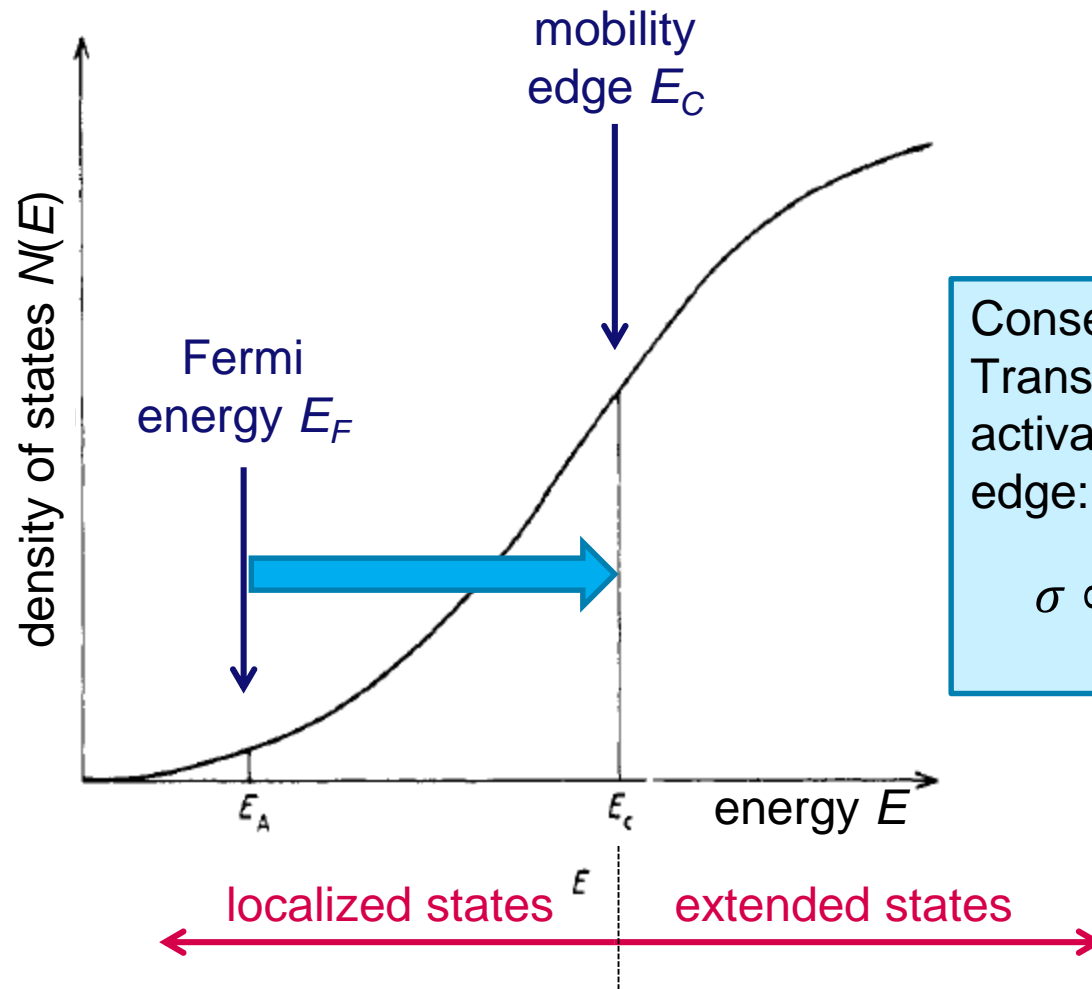
Consequence:
Transport occurs by thermal activation over the mobility edge:

$$\sigma \propto \sigma_0 \exp\left(-\frac{E_C - E_F}{k_B T} \right)$$

N.F. Mott, J. Phys. C: Solid State Phys. **20**, 3075 (1987).

Disorder – Mobility Edge model

$$\mathcal{L}^{(\alpha)} = \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon - \mu)^{\alpha}\sigma(\varepsilon)$$

mobility edge E_C

Fermi energy E_F

density of states $N(E)$

ε_A ε_c energy E

When only delocalized states contribute to charge transport: $\sigma(\varepsilon) = \sigma_0 \times \Theta(\varepsilon - E_C)$ (Heaviside step function)

And when ε_F is far below E_C (and ε): $-\frac{\partial f}{\partial \varepsilon} \approx \exp\left(-\frac{\varepsilon - \varepsilon_F}{k_B T}\right)$

Then

$$\mathcal{L}^{(0)} = \sigma \approx \sigma_0 \exp\left(-\frac{E_C - \varepsilon_F}{k_B T}\right)$$

and

$$\mathcal{L}^{(1)} \approx \sigma_0 (E_C - \varepsilon_F) \exp\left(-\frac{E_C - \varepsilon_F}{k_B T}\right)$$

So that

$$S = \frac{L_{12}}{L_{11}} = -\frac{1}{qT}\frac{\mathcal{L}^{(1)}}{\mathcal{L}^{(0)}} \approx -\frac{E_C - \varepsilon_F}{qT}$$
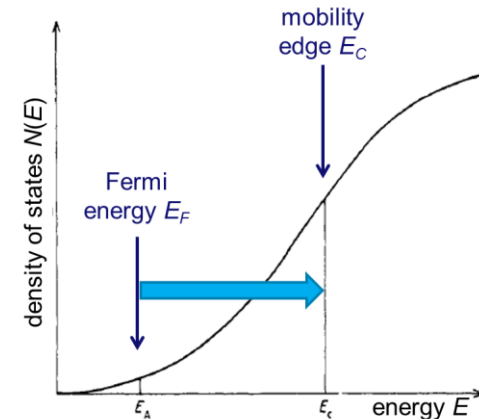
Note that σ and S are now expressed in just 2 characteristic energies!

However, there is a more transparent way to get to the same result for S….

A general expression for the thermoelectric power

Recall that (including $\frac{\partial f}{\partial \varepsilon}$ in $\sigma(\varepsilon)$):

$$\sigma = \int d\varepsilon \, \sigma(\varepsilon)$$

- The Peltier coefficient is the energy carried by the electrons per unit charge ($j^q = \Pi j$).
- Energy carried is measured relative to the Fermi energy
- Each electron contributes to Π in proportion to its relative contribution to the total conduction. The weighting factor is $\sigma(\varepsilon)/\sigma$ with $\sigma(\varepsilon)$ as defined above.

Then:

$$\Pi = -\frac{1}{q} \int d\varepsilon \, (\varepsilon - \varepsilon_F) \frac{\sigma(\varepsilon)}{\sigma}$$

which happens to be equal to $\Pi = \frac{L_{21}}{L_{11}} = -\frac{1}{q} \frac{\mathcal{L}^{(1)}}{\mathcal{L}^{(0)}}$. Using the reciprocity relation $S = \Pi/T$ one gets

$$S = -\frac{k_B}{q} \int d\varepsilon \frac{\varepsilon - \varepsilon_F}{k_B T} \frac{\sigma(\varepsilon)}{\sigma}$$

For the mobility edge case, using $\sigma(\varepsilon) \propto \Theta(\varepsilon - E_C)$ leads directly to

$$S = -\frac{E_C - \varepsilon_F}{qT} + A$$

H. Fritzsche, Solid State Comm. **9**, 1813 (1971).

Assumption: charge transport by 'jumping' between localized states

transport
energy E_t

density of states $N(E)$

equilibrium
energy E_{eq}
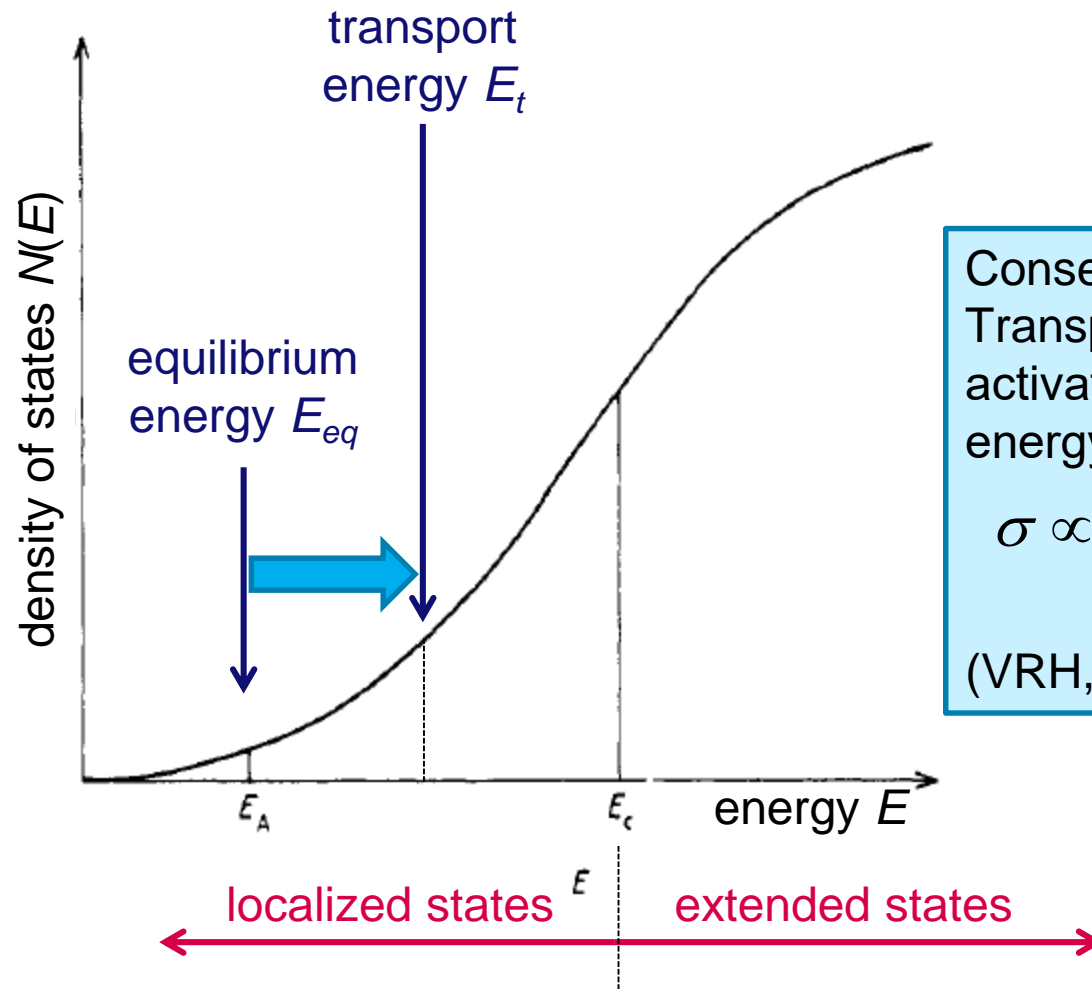
Consequence:
Transport occurs by thermal activation to a 'transport energy':

$$\sigma \propto \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^{\frac{1}{4}} \right)$$

(VRH, constant DOS, 3D)

E_A E_c energy E

E

localized states   extended states

One may anticipate $S \cong -\frac{E_t - E_{eq}}{T}$ on basis of the previous findings…

N.F. Mott, Phil. Mag. **19**, 835 (1969).

1. There is only weak electronic coupling between the sites/segments
2. Localized particles move by Miller Abrahams hopping

$$
\nu_{ij} = \begin{cases} \nu_0 f(r_{ij}) \exp\left[-\dfrac{E_j - E_i}{kT} \right] & \text{if } E_j - E_i > 0 \\[2em] \nu_0 f(r_{ij}) & \text{if } E_j - E_i < 0 \end{cases}
$$

$$
f(r_{ij}) = \exp(-2\alpha r_{ij})
$$

3. Hopping distance $r_{ij} \approx$ 1-3 nm (distance between benzene rings stacked on top of each other $\approx$ 3.5 Å). The localization radius $\alpha^{-1} \ll r_{ij}$.
4. Attempt frequency ν_0 for hopping time is related to molecular vibrations 30-3000 cm^{-1} $\approx$ 10^{12} - 10^{14} s^{-1}.
5. Assume a Gaussian/Exponential/Constant density-of-states (DOS) for the energy levels available to the carrier.

$$
g(E) = \frac{N_0}{\sqrt{2\pi}\sigma} \exp\left(-\frac{E^2}{2\sigma^2} \right)
$$

E

\# m^{-3}E^{-1}
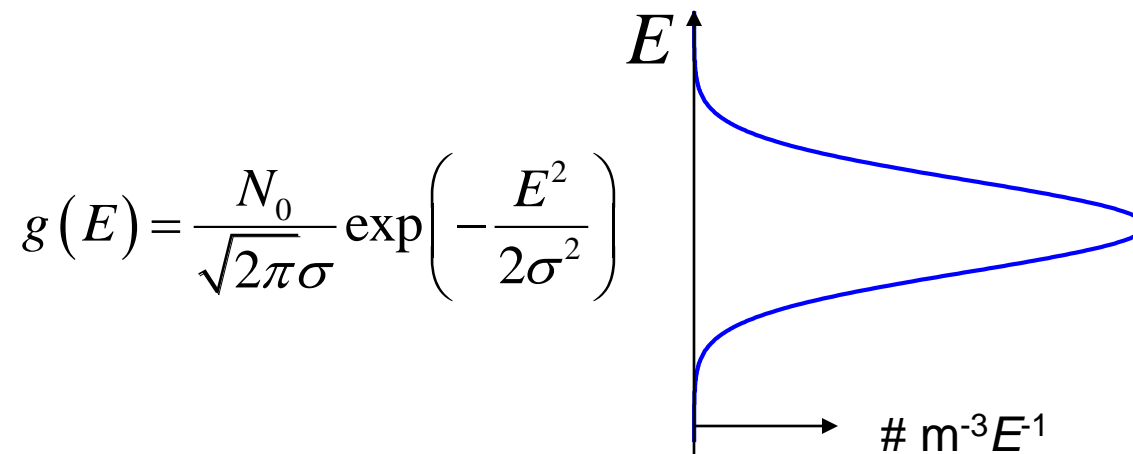
Quiz!

The simplest case: DOS = constant

- Conceptually instructive.

- Not very realistic in intrinsic organic semiconductors

- Maybe relevant some highly doped organic semiconductors (PEDOT:PSS)

Case II: DOS = Gaussian

•Partially analytically treatable.

•Very relevant in intrinsic organic semiconductors

•Here: look at T-dependence in the Boltzmann-limit (low n,p)

Thermal equilibrium: charge distribution over DOS $g(\varepsilon)$ according to Boltzmann.

*Density of occupied states (*DOOS*)*: the set of energy levels occupied by the charges (usually at thermal equilibrium).

Question: What are the average energy $\langle \varepsilon \rangle_{\infty}$ and width σ of this distribution?
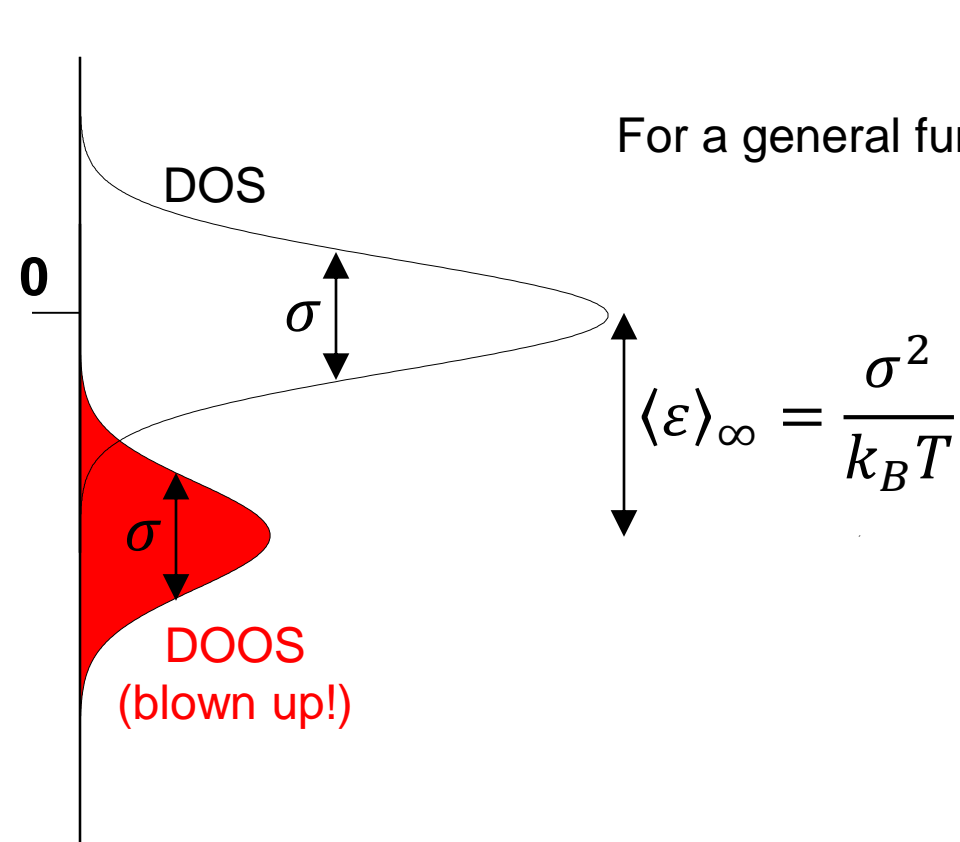
For a general function f:

$$\langle f \rangle_{\infty} = \frac{\int\limits_{-\infty}^{\infty} f(\varepsilon) g(\varepsilon) \exp\left[-\frac{\varepsilon - \varepsilon_F}{kT} \right] d\varepsilon}{\int\limits_{-\infty}^{\infty} g(\varepsilon) \exp\left[-\frac{\varepsilon - \varepsilon_F}{kT} \right] d\varepsilon}$$

DOS

0

σ

$$\langle \varepsilon \rangle_{\infty} = \frac{\sigma^2}{k_B T}$$

σ

DOOS
(blown up!)

Taking $f(\varepsilon) = \varepsilon$ gives

$$\langle \varepsilon \rangle_{\infty} = \frac{\sigma^2}{k_B T}$$

and variance

$$\mathrm{var}(\varepsilon)_{\infty} = \left\langle \varepsilon^2 - \langle \varepsilon \rangle_{\infty}^2 \right\rangle_{\infty} = \sigma^2$$

and width

$$\mathrm{std}(\varepsilon)_{\infty} = \sqrt{\mathrm{var}(\varepsilon)_{\infty}} = \sigma$$

Gaussian DOS – relaxation & transport

initially:
anomalous or *dispersive* transport
(high μ when $\varepsilon_s > \varepsilon_\infty$)

at steady state:
Gaussian transport

start energy ε_s

transport energy ε_t

equilibrium energy ε_∞

$t = 0$ hopping sequence

Baranovskii *et al.*, Phys. Rev. B **62**, 7934 (2000)
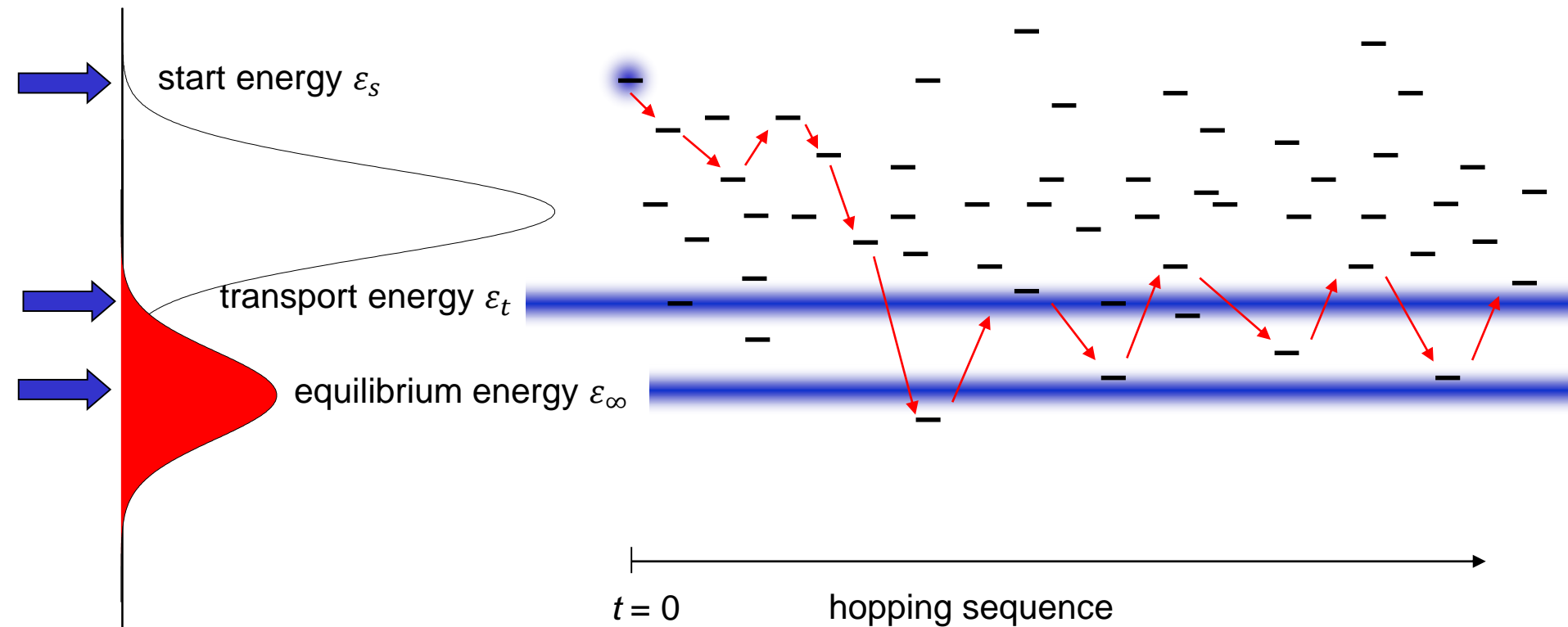
transport energy ε_t
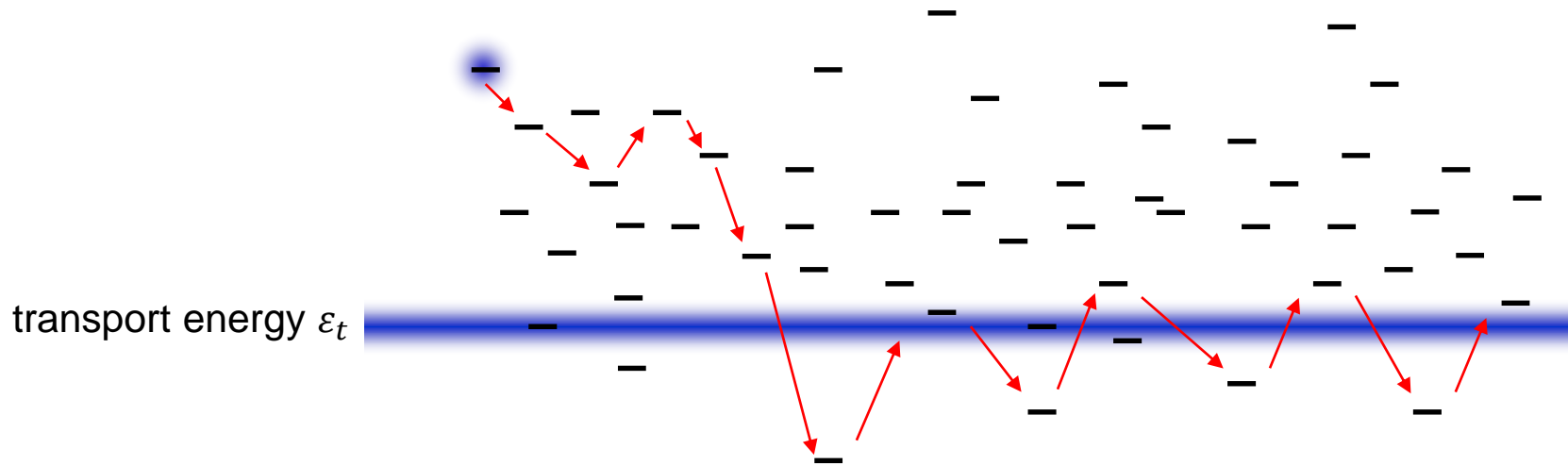
When the carrier jumps up in energy from a low energy site it faces a *dilemma*:

Jumping to high-energy sites requires more thermal energy then to low-energy sites.

but

At higher energies more states become available in close proximity

so

There is a trade-off between hopping near (to a high energy) and far (to a low energy)

$$\nu_{up}\left(\varepsilon_i, \varepsilon_f\right) = \nu_0 \exp\left[-\frac{2r_{if}}{\alpha} - \frac{\varepsilon_f - \varepsilon_i}{kT}\right]$$

Probability to jump up in energy according to Miller-Abrahams

$\varepsilon_{i/f}$:   initial/final energy level of the particle

r_{if} :   distance from initial to final site, $|r_f - r_i|$

To find the maximum of ν_{up} at a given ε_i, we need a relation between ε_f and r_{if}. We can obtain one by estimating r_{if} in the following way:

Baranovskii *et al.*, Phys. Rev. B **62**, 7934 (2000)

Within a 4D sphere (radius r, energy window ΔE) the number of sites is:

$$\# \approx r^3 \cdot \Delta E \cdot g\left(E_F\right) = B_c$$

The hopping probability (~conductivity, mobility) is

$$p \propto \exp\left(-2\alpha r\right) \cdot \exp\left(-\Delta E/kT\right)$$

Hence, keep the sphere as small as possible. Percolation theory gives $B_c = 2.8$.
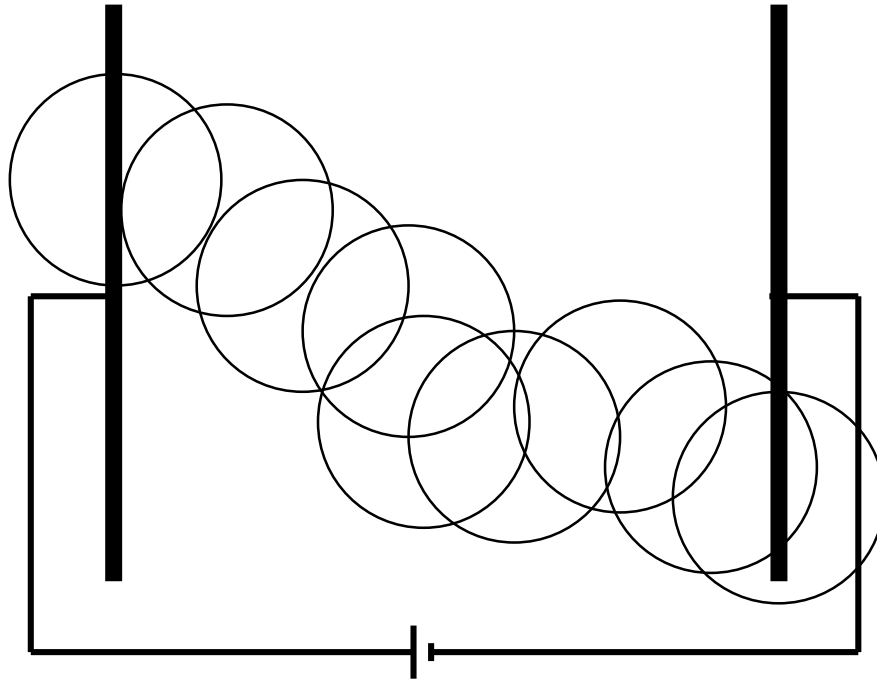
$$\nu_{up}\left(\varepsilon_i,\varepsilon_f\right)=\nu_0\exp\left[-\frac{2r_{if}}{\alpha}-\frac{\varepsilon_f-\varepsilon_i}{kT}\right]$$

Probability to jump up in energy according to Miller-Abrahams

$\varepsilon_{i/f}$: initial/final energy level of the particle

r_{if} : distance from initial to final site, $|r_f - r_i|$

To find the maximum of ν_{up} at a given ε_i , we need a relation between ε_f and r_{if}. We can obtain one by estimating r_{if} in the following way:

Since $\displaystyle\int_{-\infty}^{\varepsilon_f} g(\varepsilon)d\varepsilon$ equals the total density of states with an energy below

ε_f ([ ] = m^{-3}),

the average distance r_{av} between these sites is $\displaystyle r_{av}=\left(\frac{4\pi}{3}\int_{-\infty}^{\varepsilon_f} g(\varepsilon)d\varepsilon\right)^{-\frac{1}{3}}$.

Taking r_{av} as an approximation for r_{if}, ν_{up} can be calculated…

Baranovskii *et al.*, Phys. Rev. B **62**, 7934 (2000)

$$\nu_{up}\left(\varepsilon_i, \varepsilon_f\right) = \nu_0 \exp\left[-\frac{2r_{if}}{\alpha} - \frac{\varepsilon_f - \varepsilon_i}{kT}\right]$$

The *transport energy* is the energy that the carrier jumping up most likely jumps to, i.e. the maximum of the log[$\nu_{up}(\varepsilon_i, \varepsilon_f)$] vs. ε_f curve.

The position of this maximum is (almost) independent of ε_i !

This allows us to predict the temperature-dependence of the carrier mobility. For this, we need a relation between ν_{up} and μ…

$\varepsilon_\infty = -2$

$\varepsilon_\infty = -2.5$

$\varepsilon_\infty = -3$

T = 295 K
N = 1
σ = 1
$\nu_0 = 1$
α = 0.05

$\log[\nu_{up}(\varepsilon_i, \varepsilon_f)]$

ε_f

Baranovskii *et al.*, Phys. Rev. B **62**, 7934 (2000)
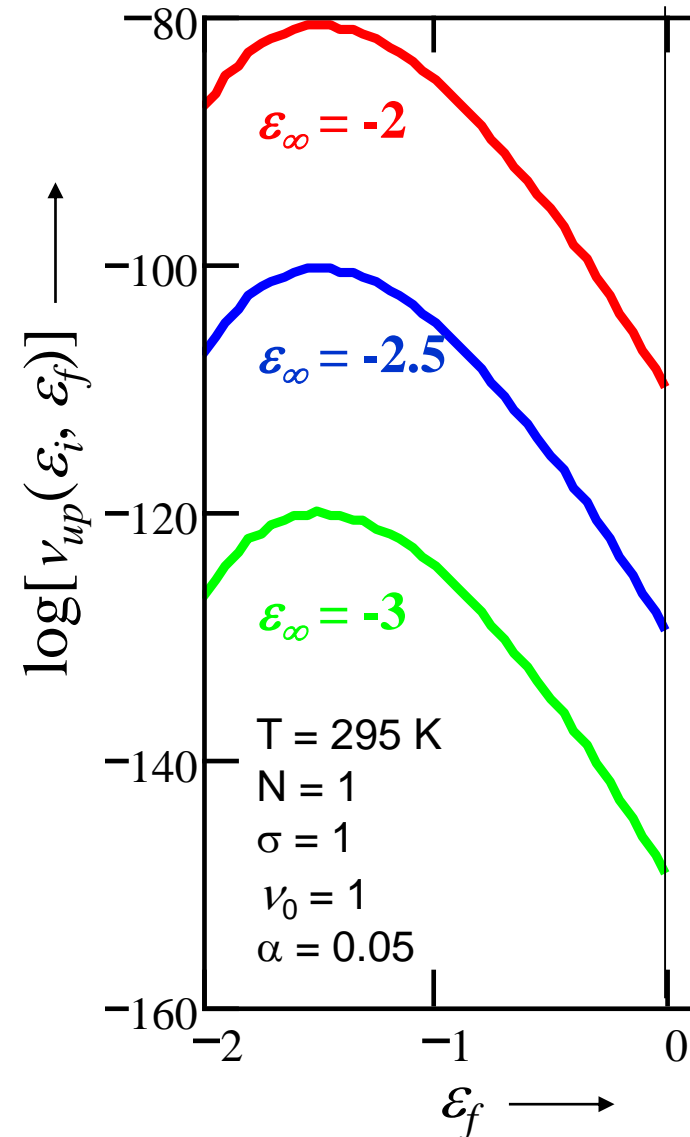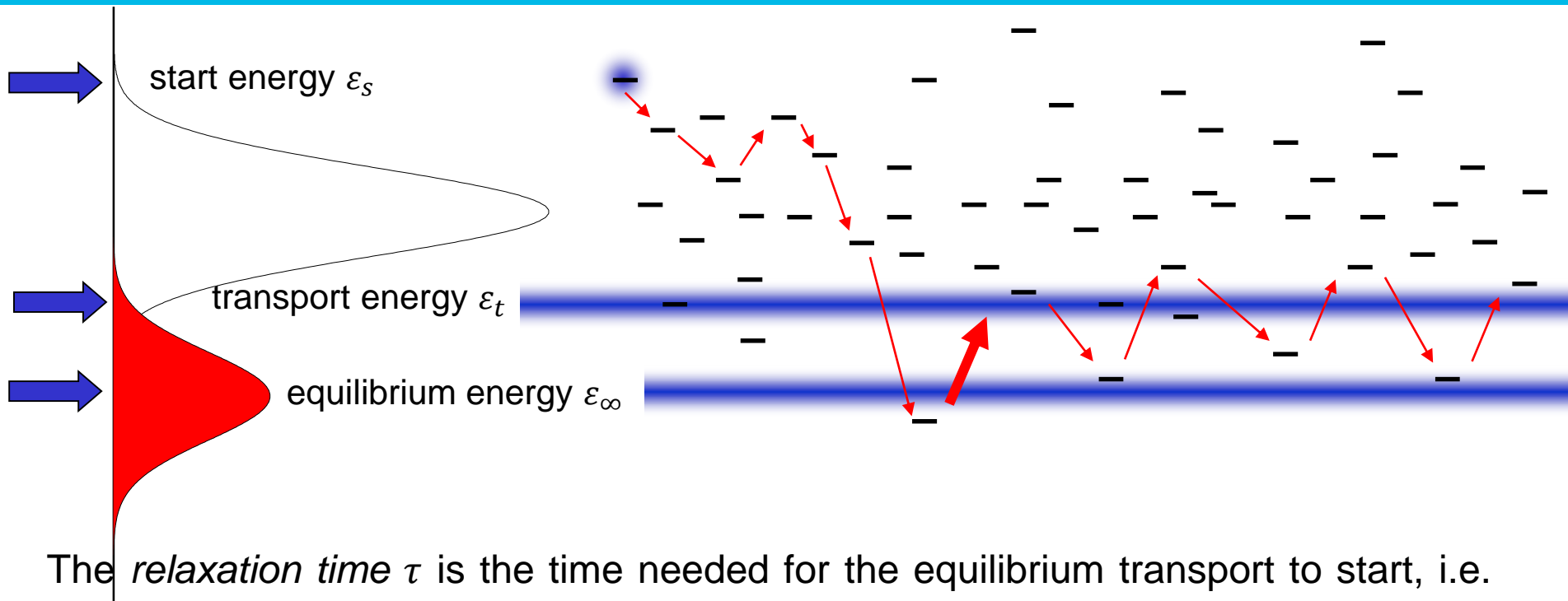
The *relaxation time* τ is the time needed for the equilibrium transport to start, i.e. the time to reach ε_t from ε_s. The rate limiting step is from ε_∞ to ε_t. This is also a typical time between two hops in equilibrium transport.

Since:

- ε_t is independent of ε_∞ (and hence r_{av} is independent of ε_∞)
- ε_∞ depends on T as $-\sigma^2/k_B T$

τ will depend on T as $\tau = v_{up}^{-1}\left(\varepsilon_\infty, \varepsilon_T\right) \propto \exp\left[\left(\dfrac{B\sigma}{k_B T}\right)^2\right]$

with $B \approx 1$. When $\sigma \gg k_B T$, τ becomes very long.

Baranovskii *et al.*, Phys. Rev. B **62**, 7934 (2000)
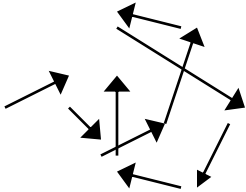
After the relaxation time, the carrier will perform a random walk with a time-independent diffusion constant *D* (Brownian motion).

Using:

$$D = \frac{d^2}{6\tau}$$

The Einstein-Smoluchowski relation
d = typical hopping distance: r_{av},
τ = average jump time

and

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

Einstein relation

we finally arrive at

$$\mu \propto \exp\left[-\left(\frac{C\sigma}{k_B T}\right)^2\right]$$

with $C \approx 0.7$.

Baranovskii *et al.*, Phys. Rev. B **62**, 7934 (2000)

DOS

0

σ

σ

DOOS

$$\langle \varepsilon \rangle_\infty = \frac{\sigma^2}{k_B T}$$
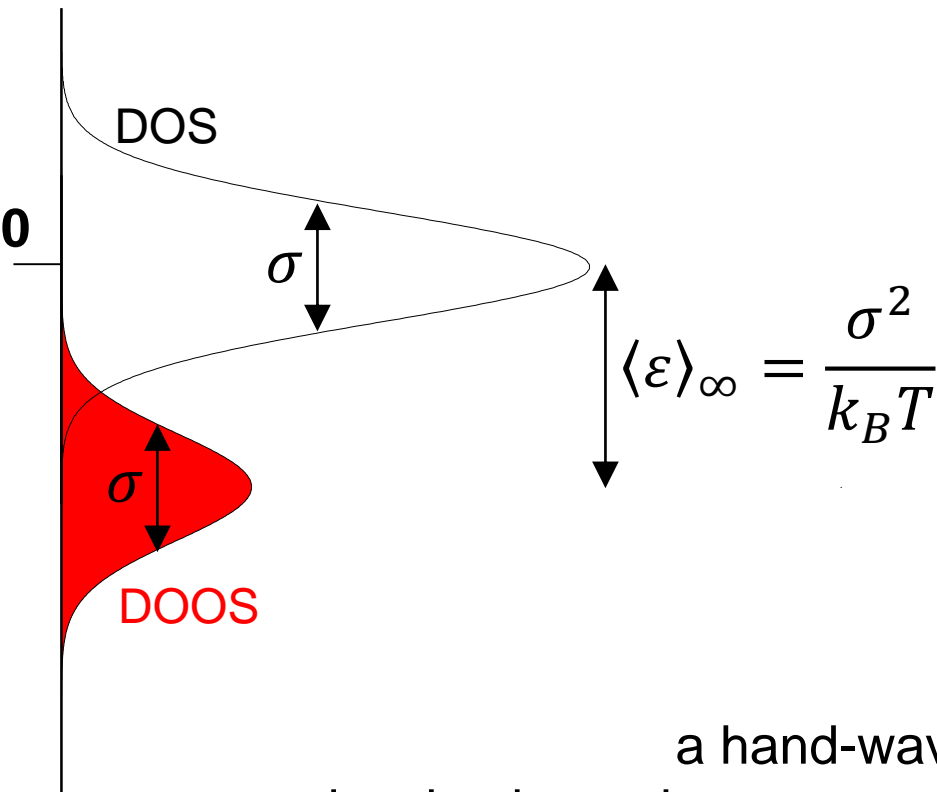
When
n is not 'small'…
or
the field is not 'small'…

The mobility will **increase**!

a hand-waving explanation:

density dependence:
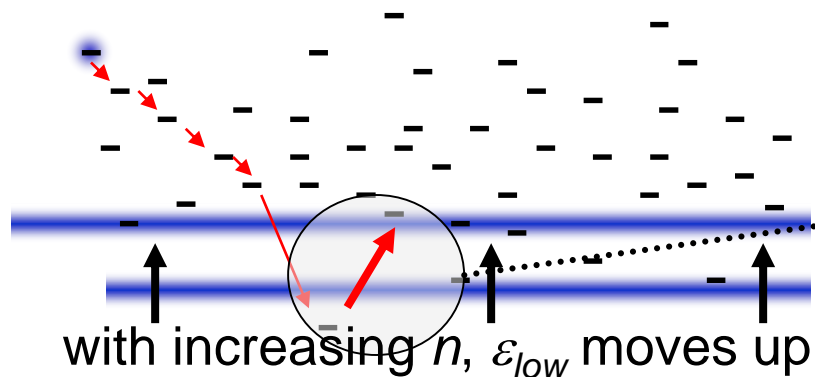
field dependence:

$\Delta E_f = eFL_{typ}$

L_{typ}

F

with increasing n, ε_{low} moves up
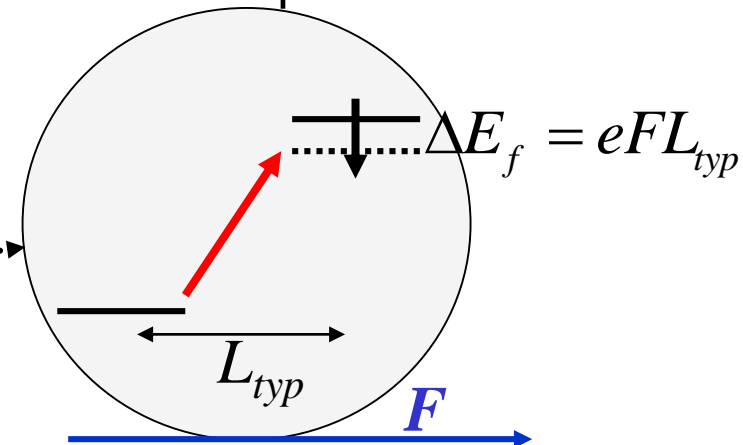
- density dependence:
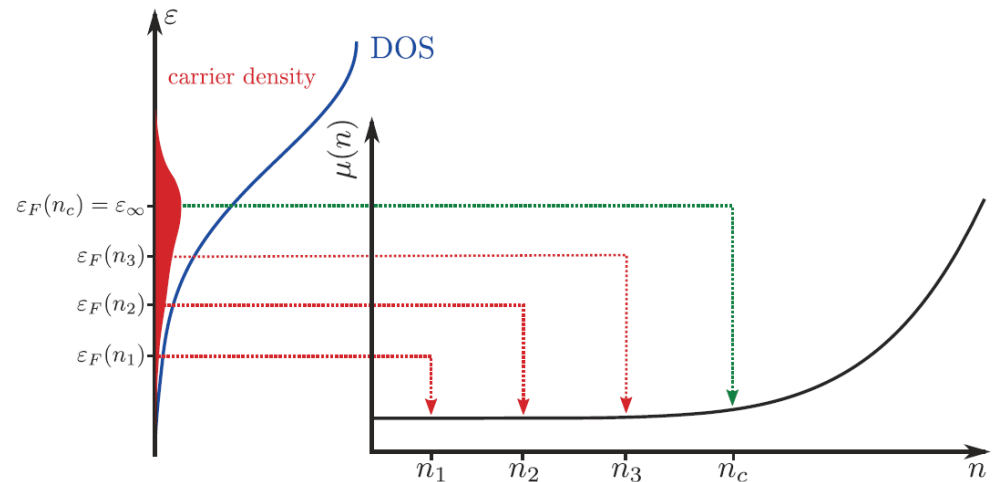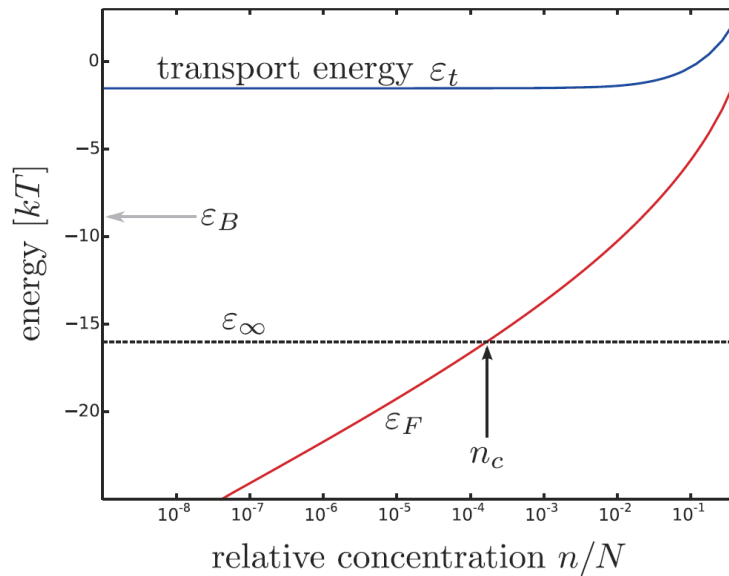
- field (F) dependence:
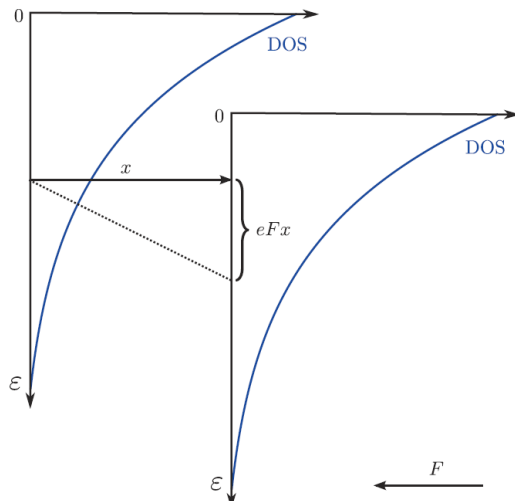
The energy picked up by hopping in the direction of a large field gives rise to an effective temperature $T_{eff} \geq T$:

$$T_{eff} = \left[T^\beta + \left(\gamma \frac{qF\alpha}{k_B} \right)^\beta \right]^{1/\beta} \quad \text{with } \beta \approx 2 \text{ and } \gamma \approx 0.67$$

S.D. Baranovskii, Phys. Status. Solidi B **251**, 487-525 (2014)
S. Marianer and B.I. Shklovskii, Phys. Rev. B **46**, 13100 (1992)
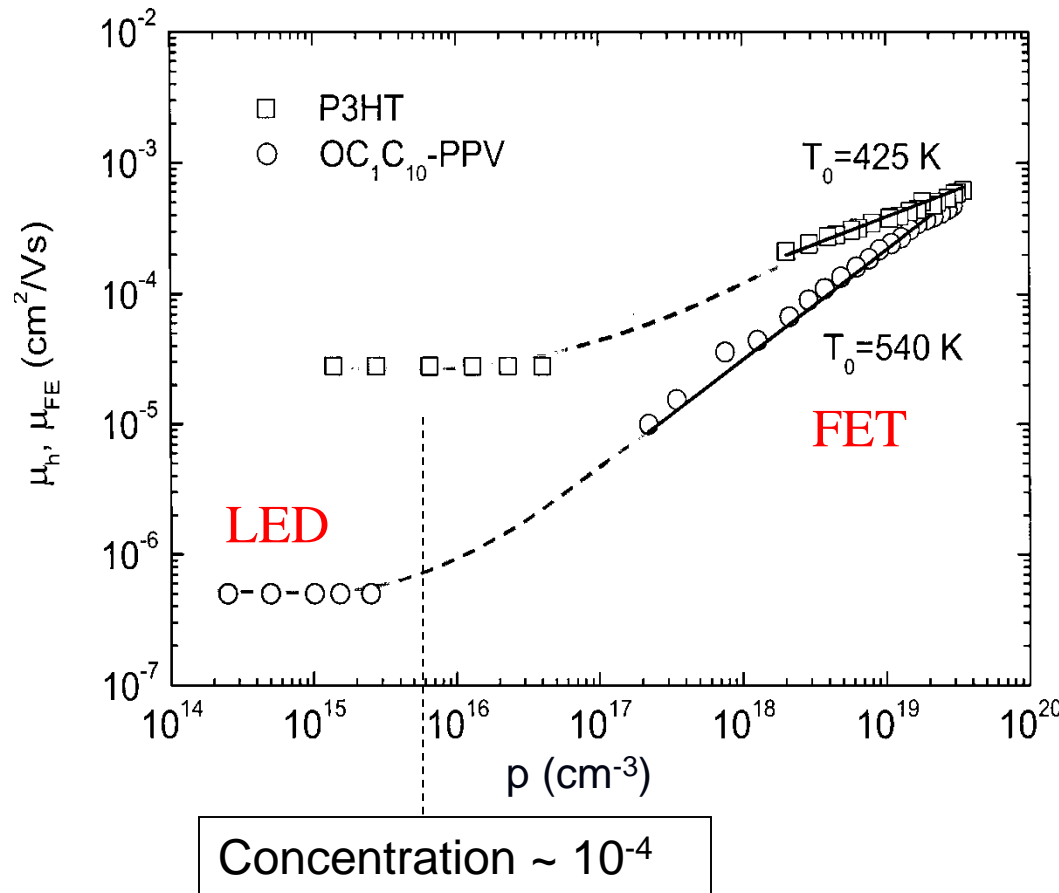
In 2003:

Good fit in FET region using a Mott-type mobility model, assuming hopping in an exponential DOS.

No explanation for the concentration independent mobility at low concentrations, observed for LEDs.

Explanation possible assuming a Gaussian DOS

Tanase et al., Phys. Rev.Lett **91**, 216601 (2003)

- Starting from

$$S = -\frac{k_B}{q}\int d\varepsilon \, \frac{\varepsilon - \varepsilon_F}{k_B T}\frac{\sigma(\varepsilon)}{\sigma}$$

and assuming that $\sigma(\varepsilon)$ is narrowly centered around ε_t (only in this case is the transport energy a relevant concept), one gets*

$$S \approx -\frac{\varepsilon_t - \varepsilon_F}{qT}$$
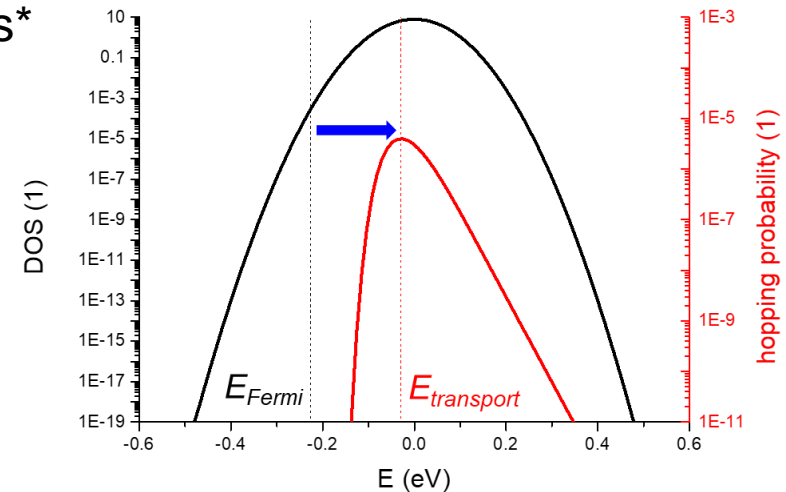
- There are several more elaborate VRH-based methods available in literature, see the Refs. below.

- Due to the concentrations of ionized dopants and charge carriers, the assumption of a purely Gaussian DOS will break down (shown later), so we need a more flexible model…

R. Schmechel, *J. Appl. Phys.* **2003**, *93*, 4653
G. Kim and K.P. Pipe, *Phys. Rev. B.* **2012**, *86*, 085208
S. Ihnatsenka et al., *Phys. Rev. B.* **2015**, *92*, 035201
N. Lu et al., *Phys. Rev. B.* **2015**, *91*, 195205

*Note the similarity to the mobility edge case that gave $S \approx -\frac{E_C - \varepsilon_F}{qT}$

Gaussian DOS – thermopower

Using kinetic Monte Carlo simulations in which S is calculated from

$$S = -\frac{k_B}{q} \int d\varepsilon \, \frac{\varepsilon - \varepsilon_F}{k_B T} \frac{\sigma(\varepsilon)}{\sigma}$$

we can compare the error made by using $S \approx -\frac{\varepsilon_t - \varepsilon_F}{qT}$. Especially for the nearest neighbor hopping (nnH) case the error is very small.
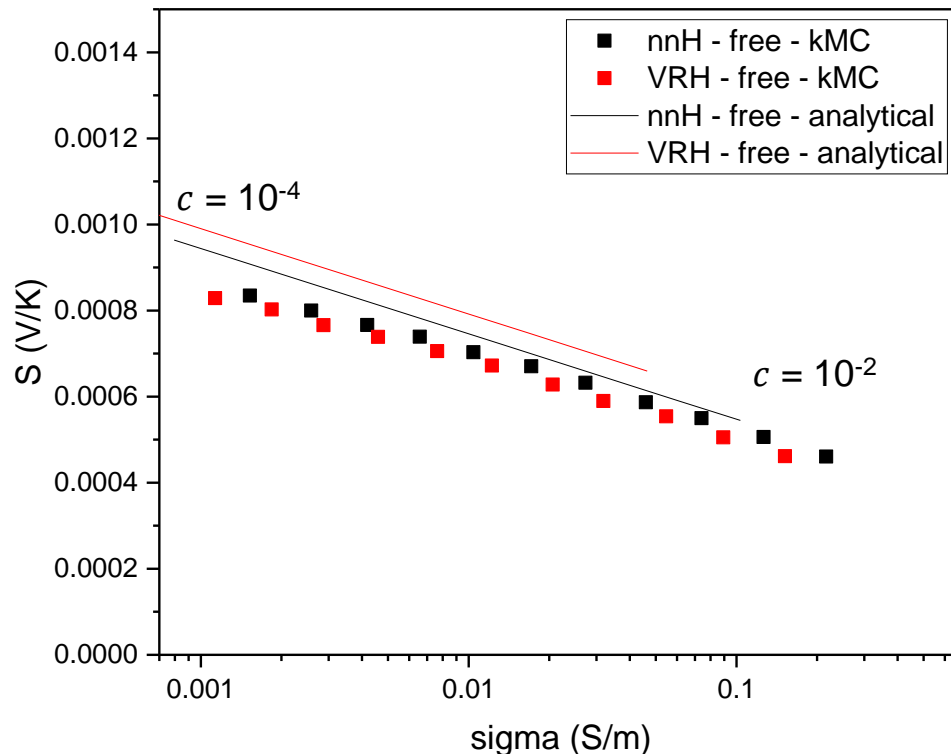
parameters used:
σ_{DOS} = 60 meV
ε_r = 3.6
T = 300 K
α^{-1} = 0.36 nm
ν_0 = 10^{11} s^{-1}
c = 10^{-4} … 10^{-2}

nnH:
simple cubic lattice, a_{NN} = 1.8 nm

VRH:
random lattice, $\overline{a_{NN}}$ = 1.8 nm

Details on the analytical model will follow below.

Outline

- Introduction: metrics for (organic) thermoelectrics
    - ZT
    - $/Watt

- Fundamentals of charge and energy transport
    - Boltzmann transport equations
    - metallic systems

- Charge transport in organic semiconductors
    - energetic disorder
    - mobility edge model
    - hopping models & percolation
        - constant DOS
        - Gaussian disorder model (GDM)

- **Beyond GDM**
    - **transport edge model**
    - **DOS design**
        - **role of dopant ions**
        - **semiconductor blends**

A universal $S \propto \sigma^{-1/4}$ relation is observed, but…

…cannot be described by 'known' models

…why is this (quasi) universal?
- morphology?
- energetics?

…how about n-type materials?
- suggested not to hold in
DOI: 10.1002/adma.201701641.

…evident relation to maximum obtainable ZT

$$ZT = \frac{\sigma S^2}{\kappa} T = \frac{PF}{\kappa} T$$
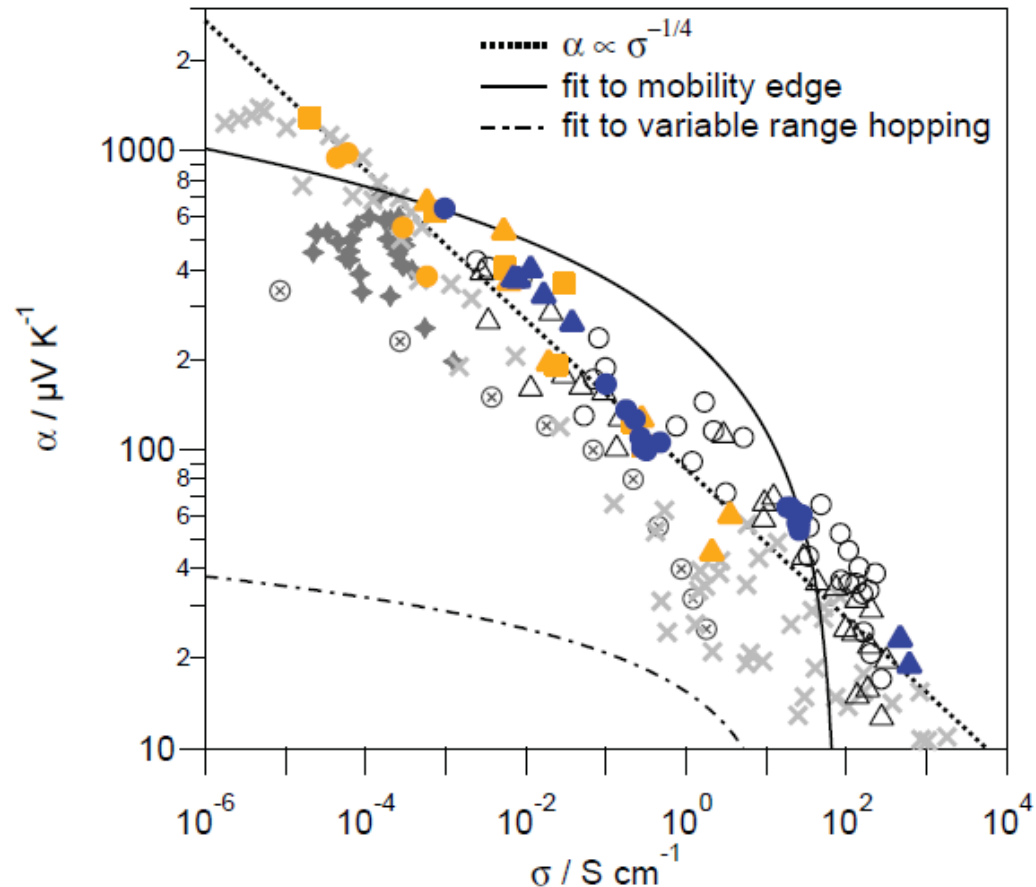
Starting from the common expression

$$\sigma = \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) \sigma(\varepsilon)$$

Kang and Snyder define an empirical transport function as

$$\sigma_E(E,T) = \sigma_{E_0}(T) \times \left(\frac{E - E_t}{k_B T} \right)^s \quad (E > E_t)$$

$$\sigma_E(E,T) = 0 \quad (E < E_t)$$
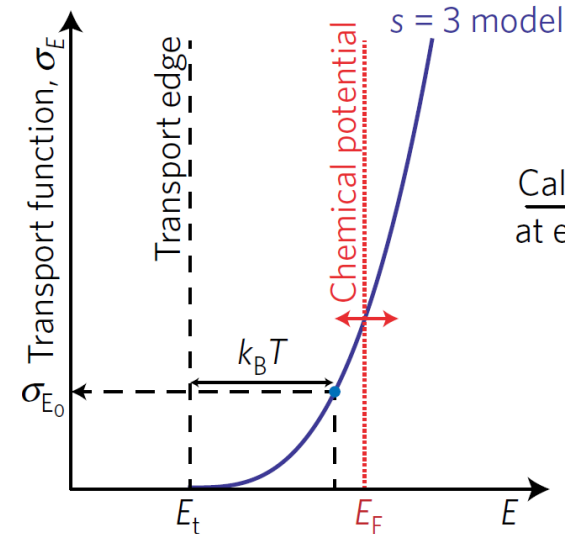
Although it fits experiments well, the physical meaning of the model and its parameters is unclear.
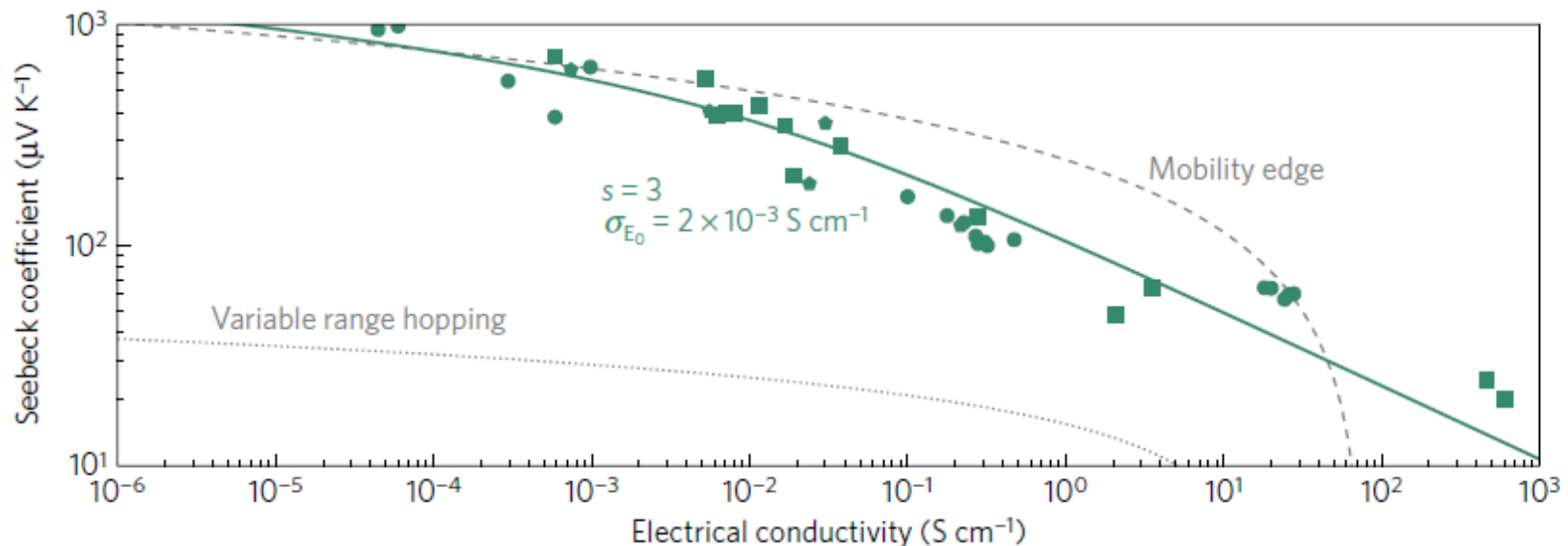
$s = 3$ model

Transport function, σ_E

Transport edge

Chemical potential

$k_B T$

σ_{E_0}

E_t E_F E

$s = 3$
$\sigma_{E_0} = 2 \times 10^{-3}$ S cm^{-1}

Mobility edge

Variable range hopping

Seebeck coefficient (μV K^{-1})

Electrical conductivity (S cm^{-1})

S.D. Kang, G.J. Snyder, *Nature Mater.* **2016**, *16*, 252-257

1. Transport edge model

2. Unintentional density of states (DOS) design: doping

    a.   universal $S \propto \sigma^{-1/4}$ relation

    b.   superior n-type thermoelectrics?

3. Intentional DOS design: blending

    a.   high (S ≈ 2000 µV/K) electronic Seebeck coefficient

    b.   role of morphology

4. Conclusions
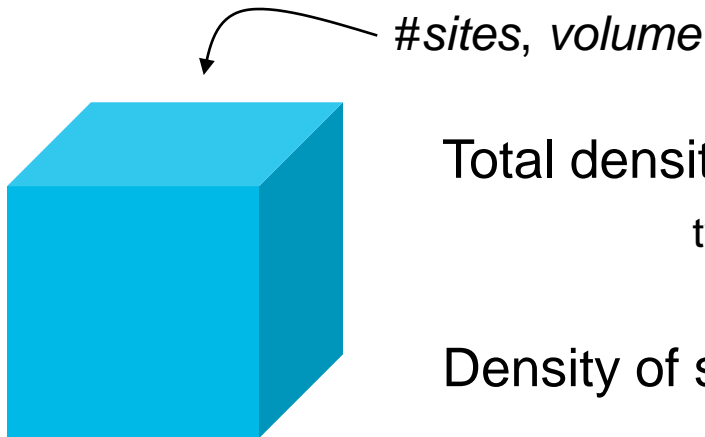
#sites, *volume*

Total density of states: $N_t = \dfrac{nr.\,of\ sites}{volume}$ (m^{-3})

typical value: 1 per 1-10 nm^{-3} → 10^{26}-10^{27} m^{-3}

Density of states: $g(E) = \dfrac{nr.\,of\ sites}{volume \times energy}$ (eV^{-1}m^{-3})

Typical DOS shapes: Gaussian   exponential

$g(E)$

σ = 0.05-0.15 eV

T_0 = 400-1000 K

energy (eV)   *energy (eV)*
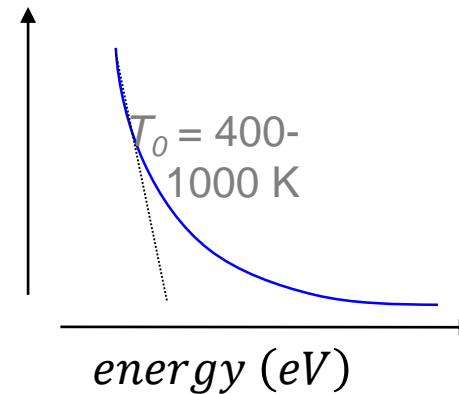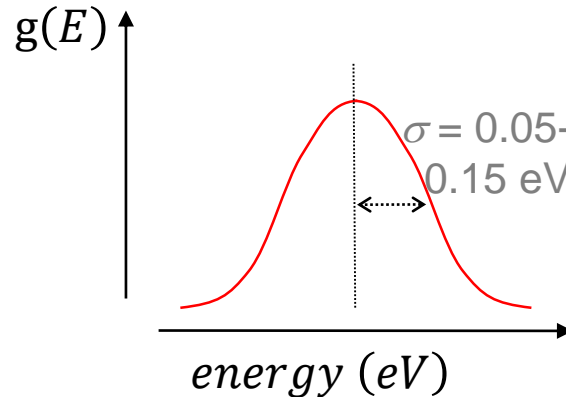
But: DOS shape can be more complicated and can be designed:

DOS – property relations!

ON THE ORIGIN OF EXPONENTIAL BAND TAILS IN AMORPHOUS SEMICONDUCTORS

M. Silver

Department of Physics and Astronomy, University of North Carolina
Chapel Hill, North Carolina 27599, USA

L. Pautmeier and H. Bässler
Fachbereich Physikalische Chemie, Philipps Universität
D 3550 Marburg FRG
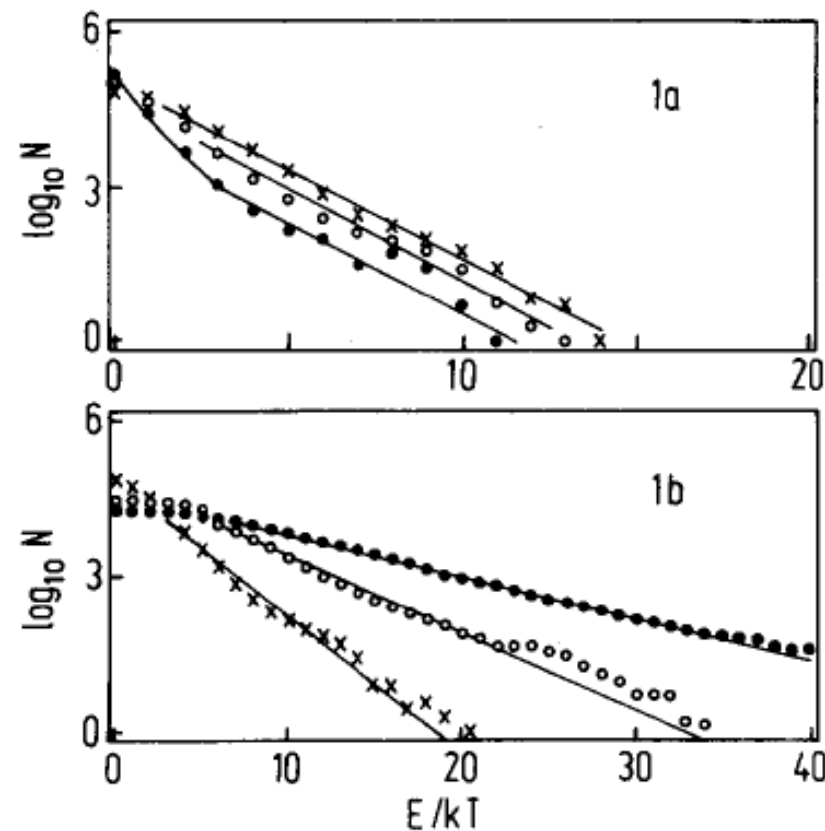
Ions induce an exponential tail of traps with a slope T_0 that depends on ε_r and a_{NN} but *not* on concentration or T.

Effect of doping on the density-of-states distribution and carrier hopping in disordered organic semiconductors

V. I. Arkhipov and P. Heremans

IMEC, Kapeldreef 75, B-3001 Heverlee-Leuven, Belgium

E. V. Emelianova

Semiconductor Physics Laboratory, University of Leuven, Celestijnenlaan 200D, B-3001 Heverlee-Leuven, Belgium

H. Bässler

$N_d = 10^{19}$ cm^{-3}
$N_d = 10^{18}$ cm^{-3}
$N_d = 10^{17}$ cm^{-3}
Intrinsic DOS

$N_i = 10^{21}$ cm^{-3}
$\sigma = 0.08$ eV
$\varepsilon = 3$
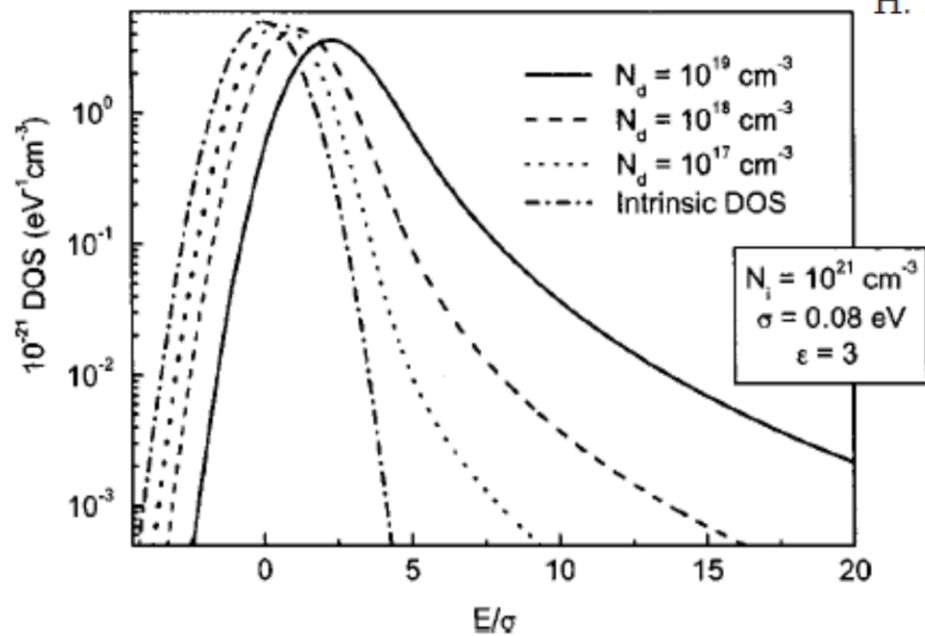
Dopant ions induce deep tail of traps.

FIG. 1. The effect of doping on the DOS distribution in a disordered organic semiconductor. The Coulomb interaction between ionized dopants and charge carriers creates additional deep traps and broadens the deep tail of the DOS.

Beyond GDM | hopping model (VRH)

$$\sigma = \sigma_0 \exp\left(-2\alpha R^* - \frac{E^* - E_F}{k_B T}\right)$$

Miller-Abrahams hopping

$$B_C = \frac{4}{3}\pi R^* \int_{E_F}^{E^*} \boldsymbol{g}(\boldsymbol{E})\,dE$$

$$E^* = \text{constant}; \text{R}^* = \text{constant}$$

Percolation criterion $\begin{cases} \text{(3D VRH)} \\ \\ \text{(3D nnH)} \end{cases}$

$$g_i(E) = \frac{N_i}{\sqrt{2\pi}\sigma_{DOS}} \exp\left(-\frac{(E - E_i)^2}{2\sigma_{DOS}^2}\right)$$

Unperturbed DOS (Gaussian)

$$g(E) = A \int_{-\infty}^{0} \frac{dE_C}{E_C^4} \exp\left(\frac{A}{3E_C^3}\right) g_i(E - E_C)$$

Ion-perturbed DOS

$$E_C(r) = -q^2 / 4\pi\varepsilon_0\varepsilon_r r$$

Coulomb energy

$$S = \frac{E^* - E_F}{qT}$$

Thermopower (holes)

Zuo et al., *Phys. Rev. B.* **2016**, *93*, 235203
Zuo et al., *J.Phys. Chem. C.* **2017**, *121*, 7767–7775

$\sigma_{DOS} =$
0.05 eV
0.075 eV
0.10 eV
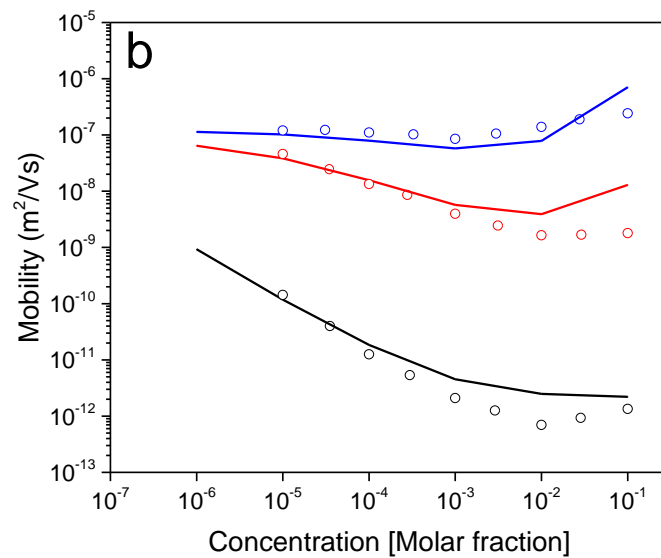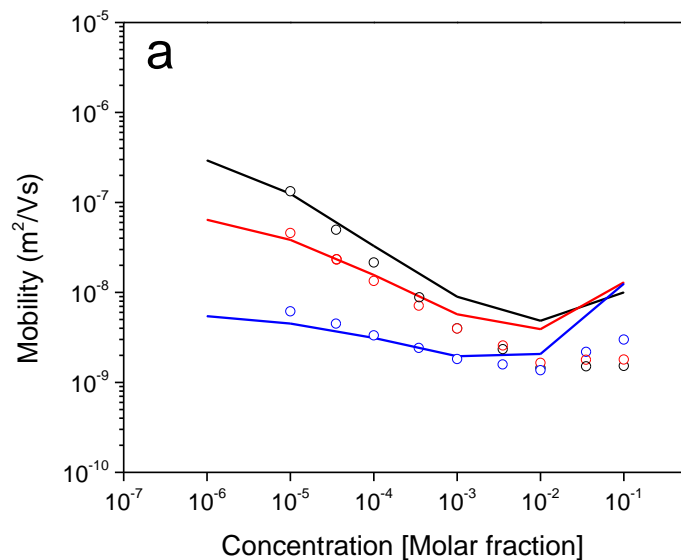
$\Delta E =$
0.30 eV
0.0 eV
-0.2 eV

$T =$
340 K
…
200 K

o o o o o : kMC

———— : analytical model

Comparison of numerical and analytical modeling:
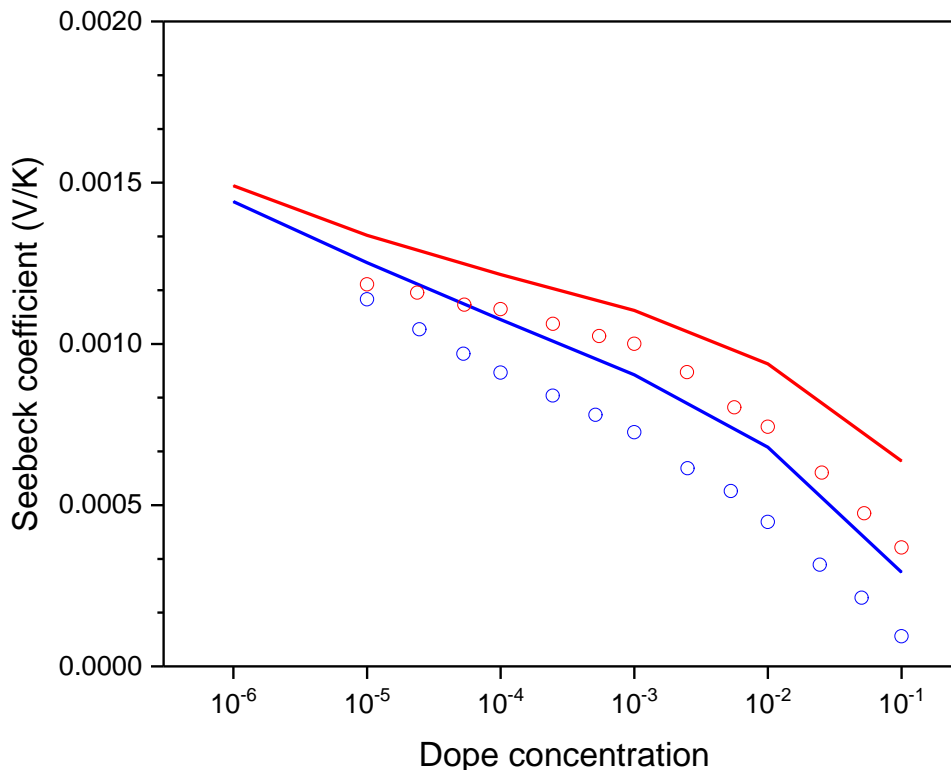
parameters used:
σ_{DOS} = 75 meV
ε_r = 3.6
T = 300 K
$\nu_0 = 10^{11}$ s^{-1}
$HOMO_{osc}$ = -5.2 eV
$LUMO_{acc}$ = -5.2 eV (red)
                    -5.5 eV (blue)

nearest neighbor hopping on
simple cubic lattice, a_{NN} = 1.8 nm

As for the case w/o Coulomb interactions, the error is relatively small.

o o o o o   : kinetic Monte Carlo model
──────   : analytical model
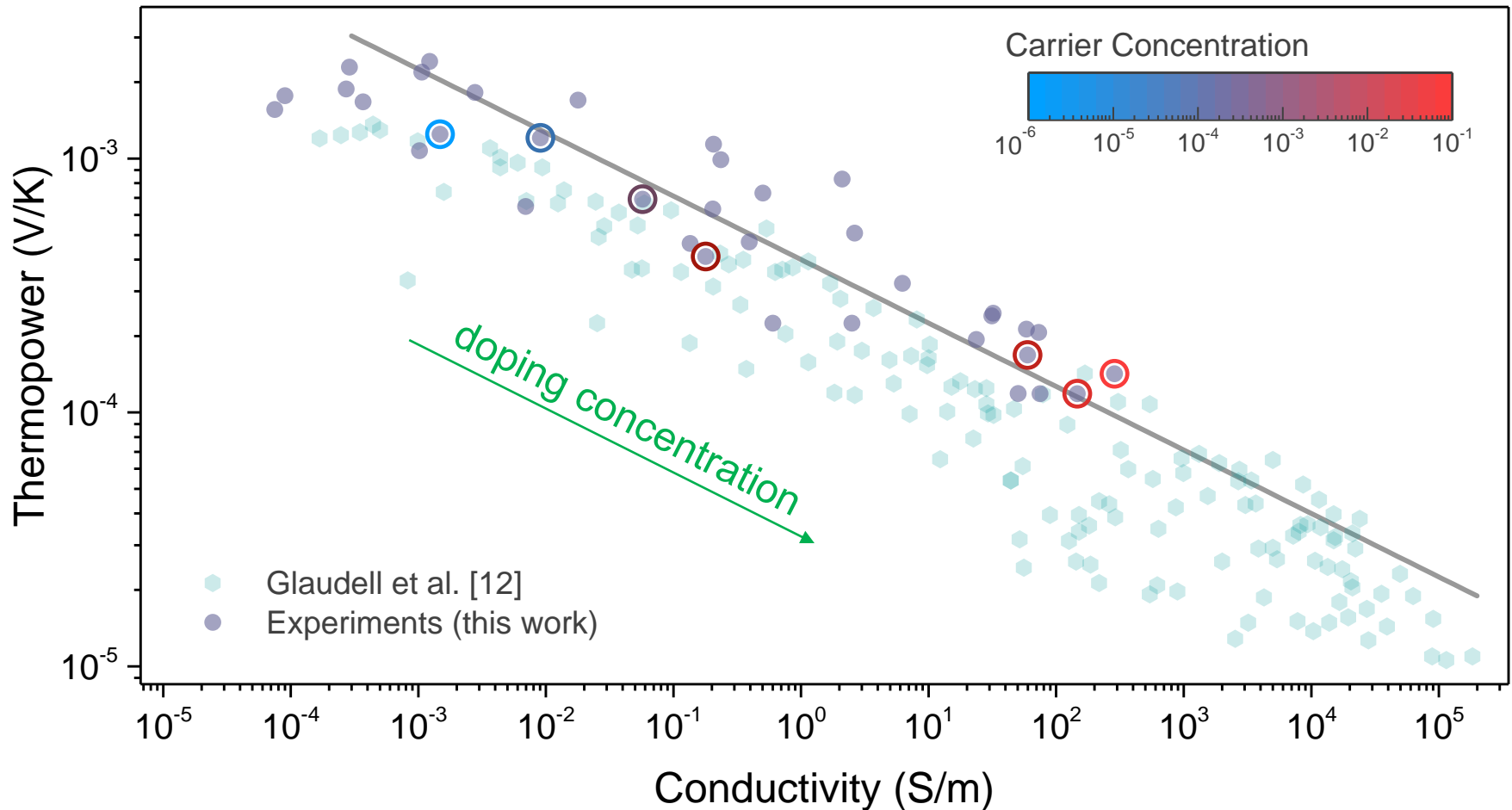
- Empirical power law with slope -1/4 is reproduced
- Materials: F_4TCNQ-doped P3HT, PCPDTBT, PTB7, MEH-PPV and P3HT:PTB7 blends (10^{-4}-10^{-1} molar) & I_2-doped PPV.
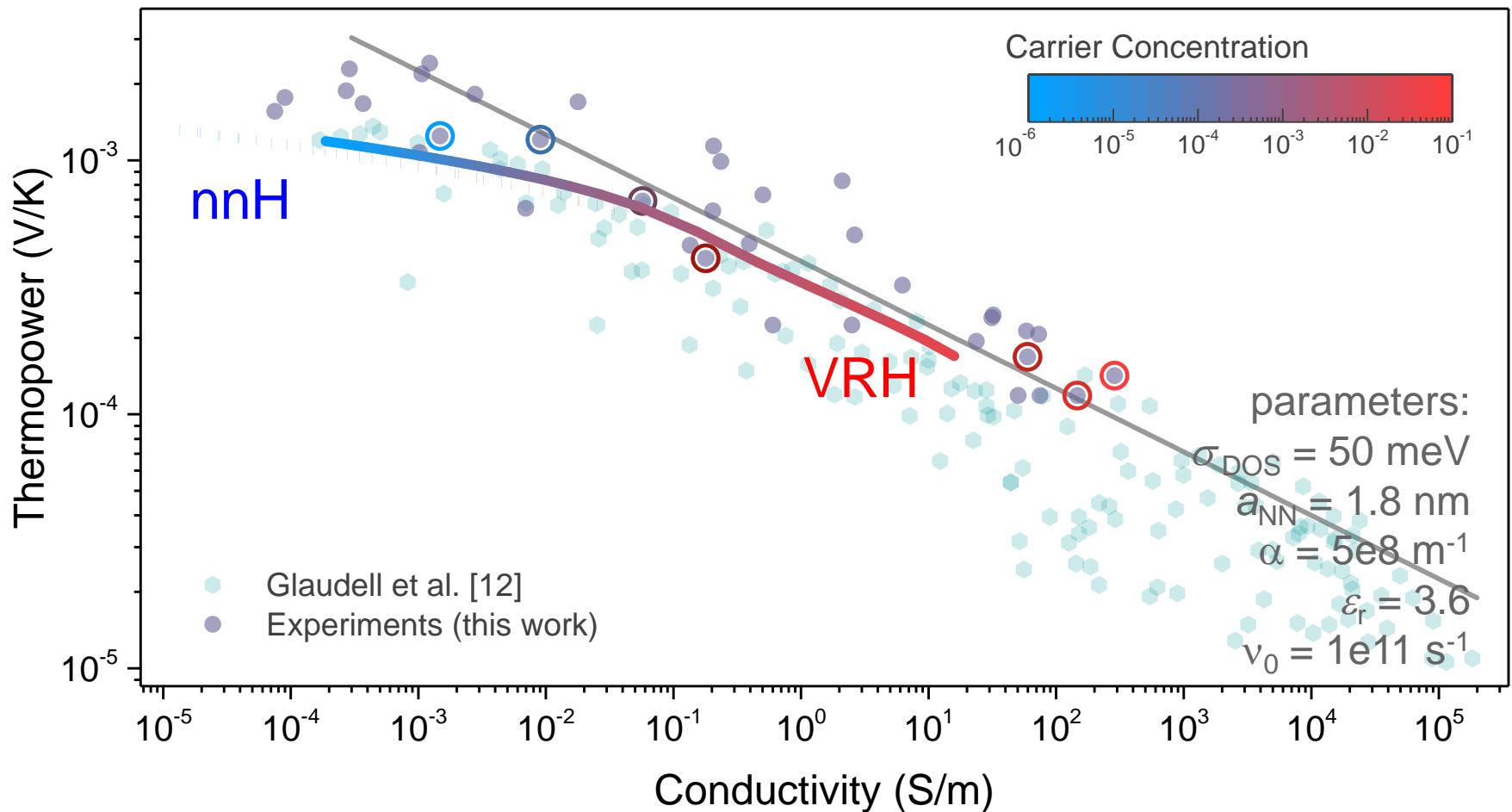
☺ Power law behavior is reproduced
☺ Slope is (virtually) independent of parameters
☺ Slope ~1/4 is consistent with experiment
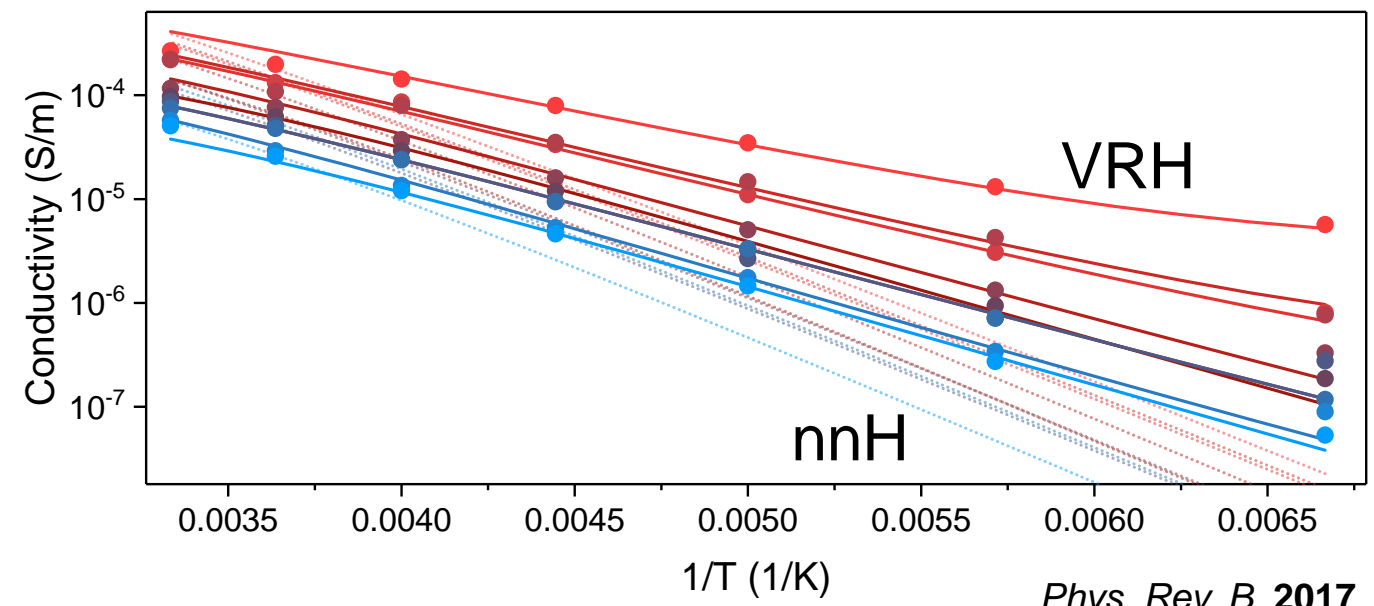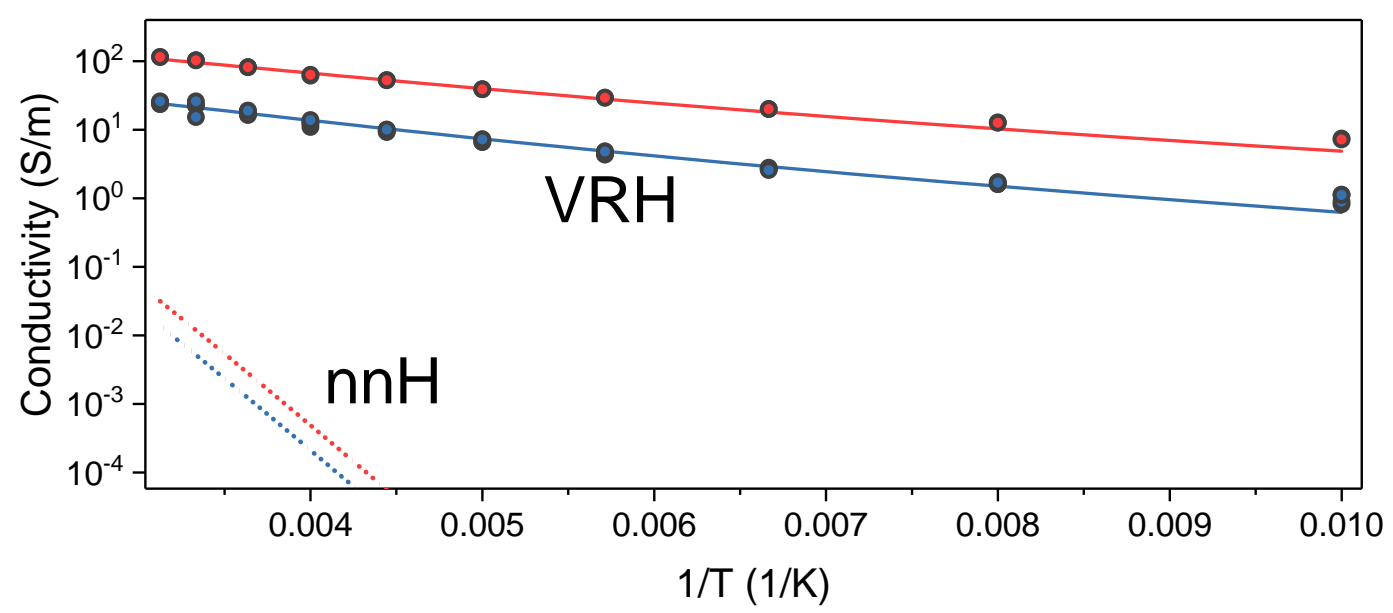
N-DPBI

PCBM

SOMO   -2.36

LUMO   -4.00

HOMO   -4.67
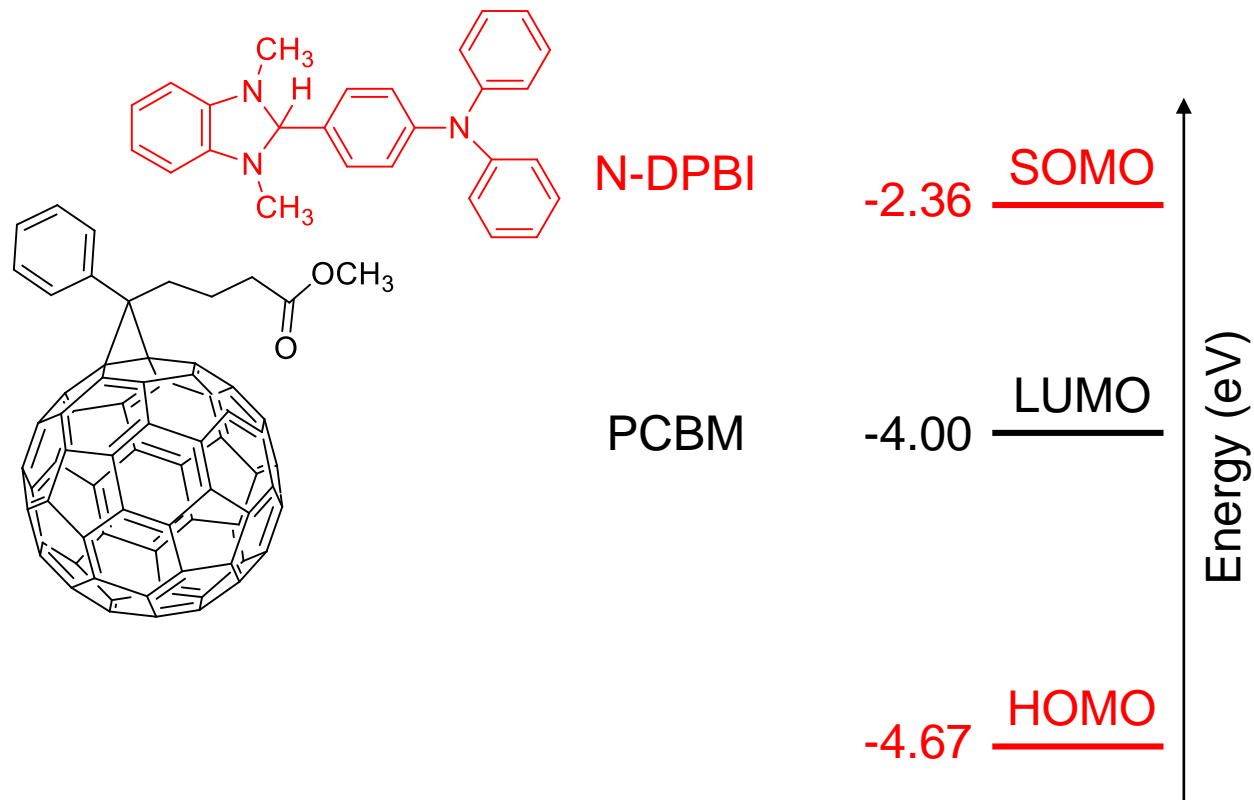
Energy (eV)
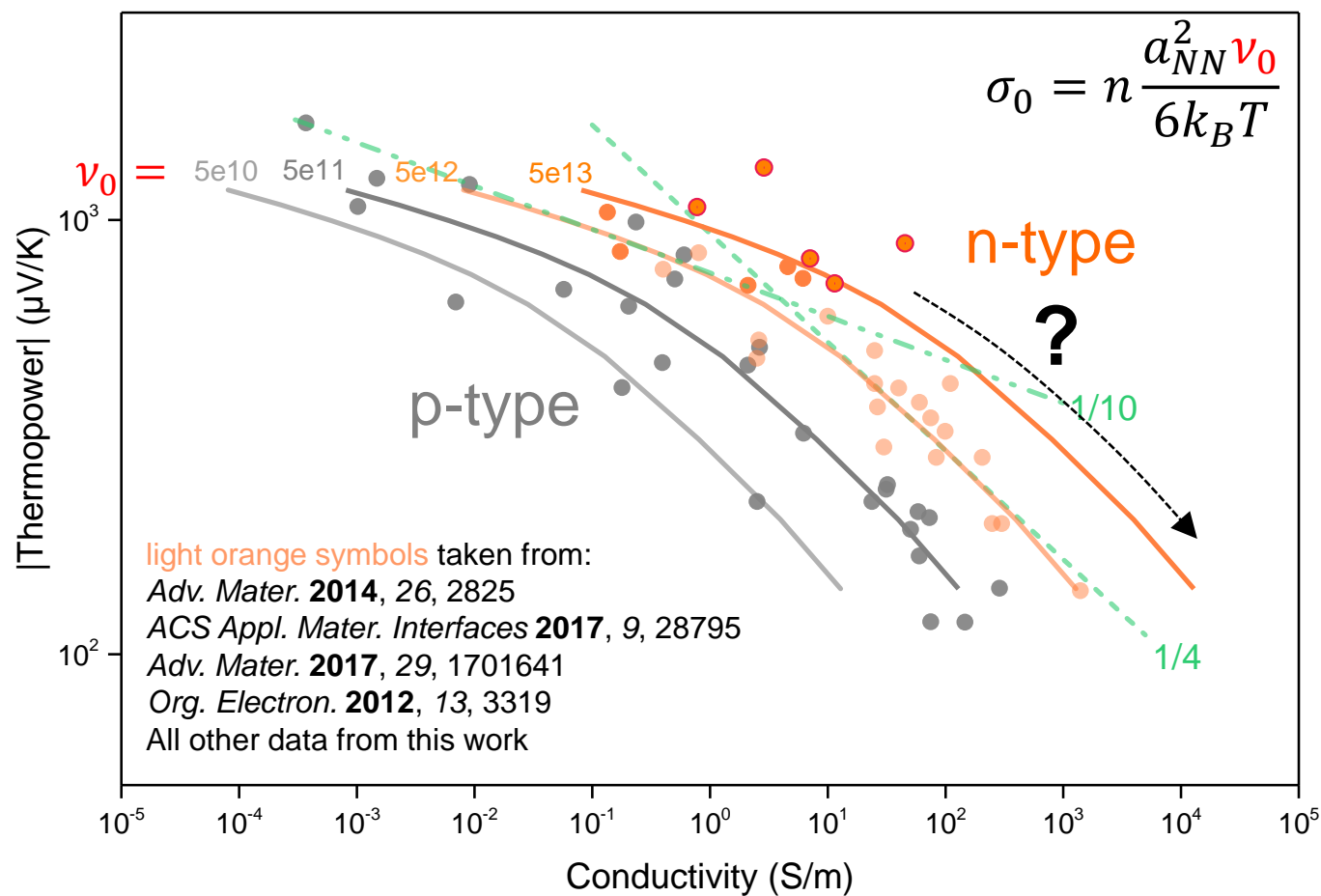
n-type thermoelectrics…
- follow 'universal' power law
- have a higher attempt-to-hop frequency ν_0!
  (see also DOI: 10.1002/aenm.201602143)

gray lines:

$$ZT = \frac{\sigma S^2}{\kappa} T \rightarrow S = \sqrt{\frac{\kappa ZT}{\sigma T}}$$

with

$$\kappa = \kappa_e + \kappa_l$$

$$\kappa_e = \left(\frac{k_B}{q}\right)^2 L\sigma T$$

$$L = L_0 = \frac{\pi^2}{3}$$
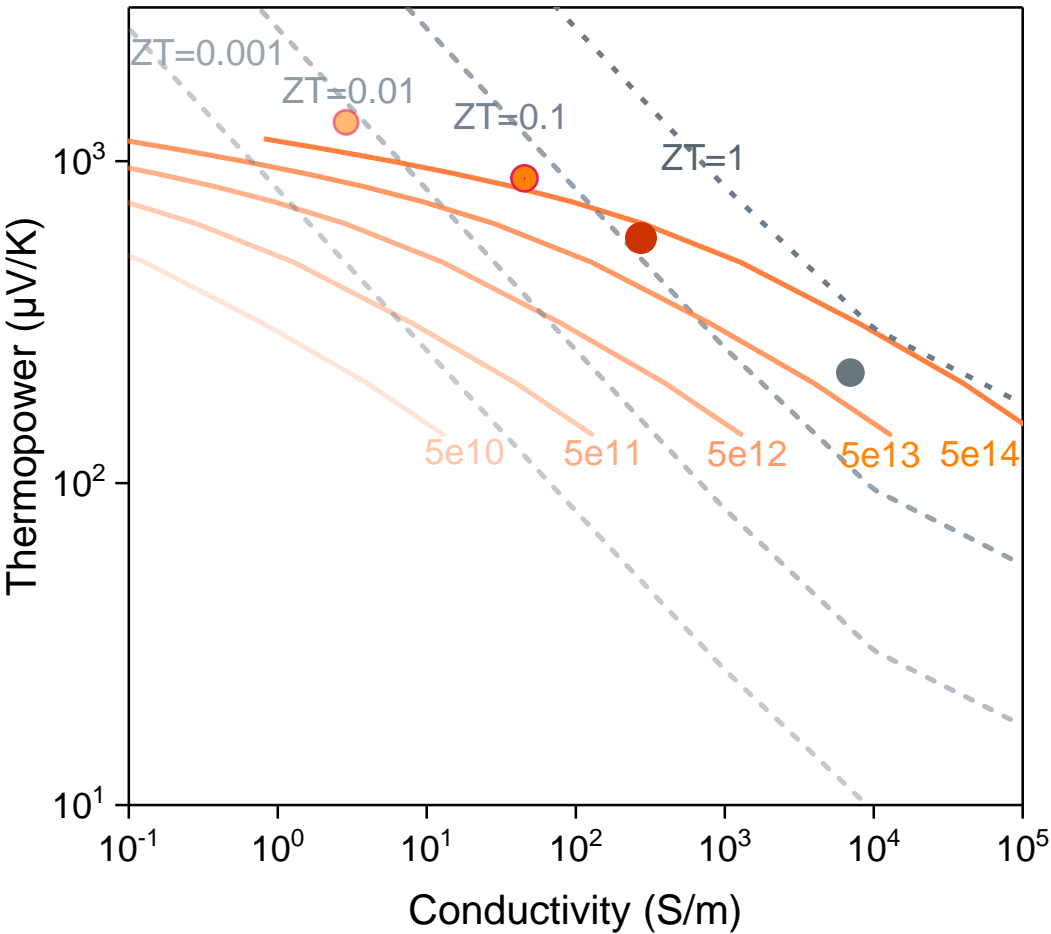
- ● highest S (n-type, this work)
- ● highest PF (n-type, this work)
- ● N-DMBI-doped A-DCV-DPPTT (n-type, *J. Am. Chem. Soc.* **2017**, *139*, 13013); ZT≈0.11
- ● PEDOT:ToS (p-type, *Nat. Mater.* **2011**, *10*, 429); ZT≈0.25

How to increase ZT?

- Increase doping ------>
  (increase σ, lower S)
- DOS design ------>
  (increase S, constant σ)
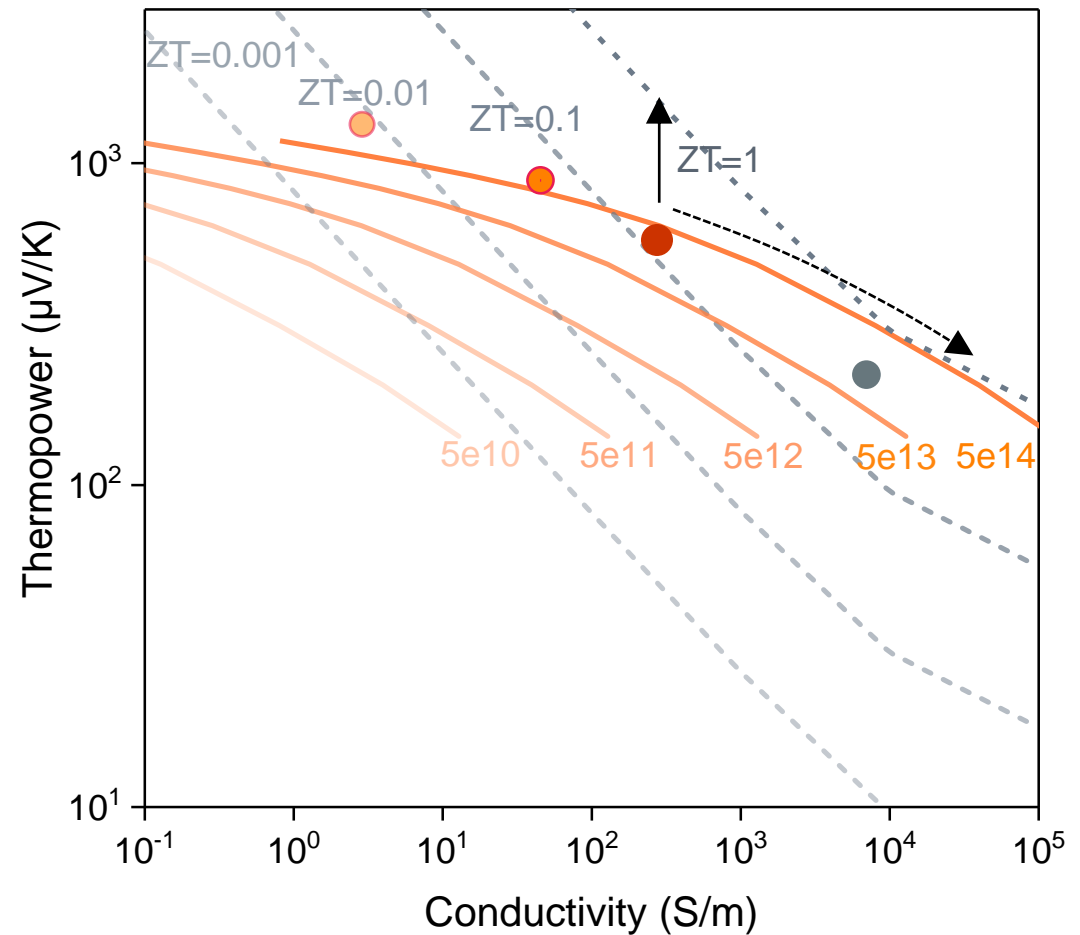
Next…

1. Transport edge model

2. Unintentional density of states (DOS) design: doping

    a. universal $S \propto \sigma^{-1/4}$ relation

    b.   superior n-type thermoelectrics?

3. Intentional DOS design: blending

    a. high (S ≈ 2000 µV/K) electronic Seebeck coefficient
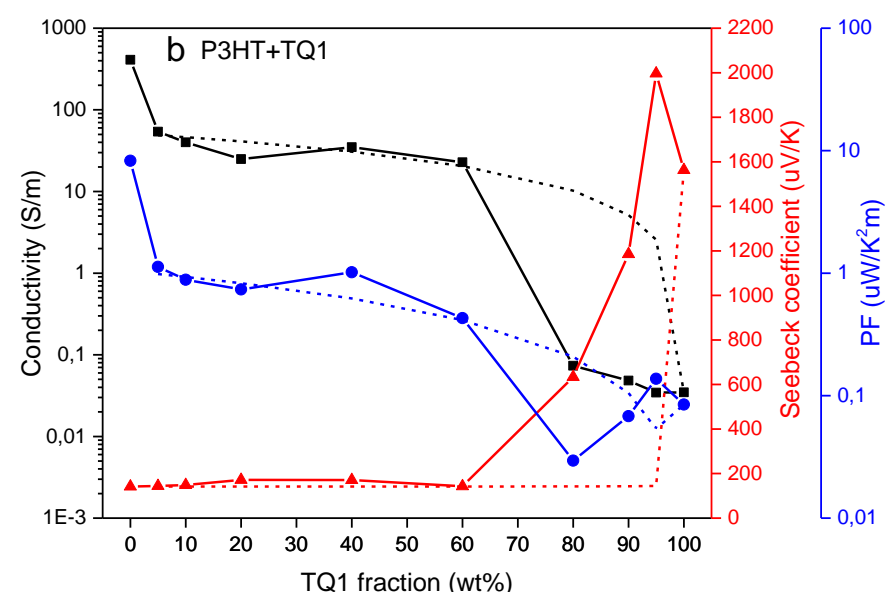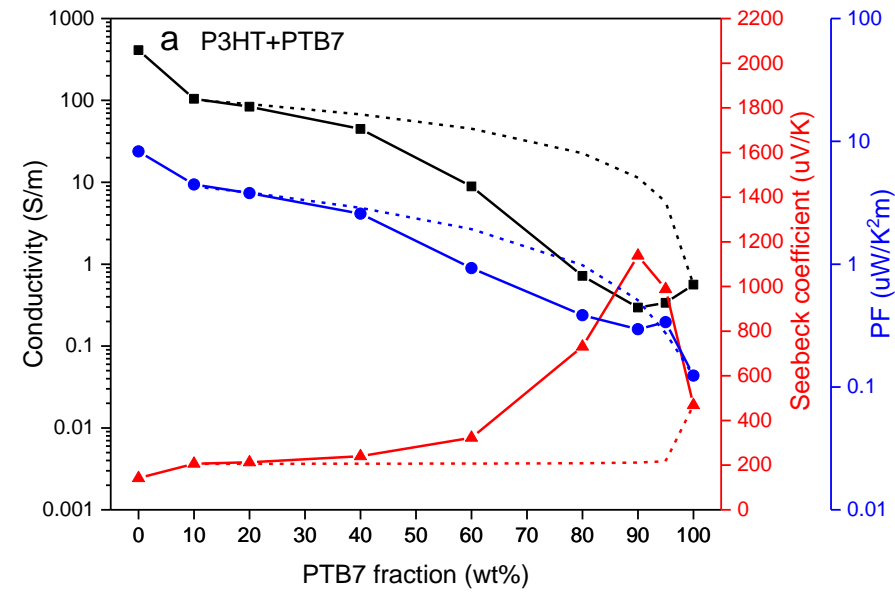
    b. role of morphology

4. Conclusions

LINKÖPING
UNIVERSITY

G. D. Mahan, J. O. Sofo, *Proc. Natl. Acad. Sci.* **1996**, *93*, 7436

H. E. Katz, *Macromolecules* **2010**, *43*, 2897
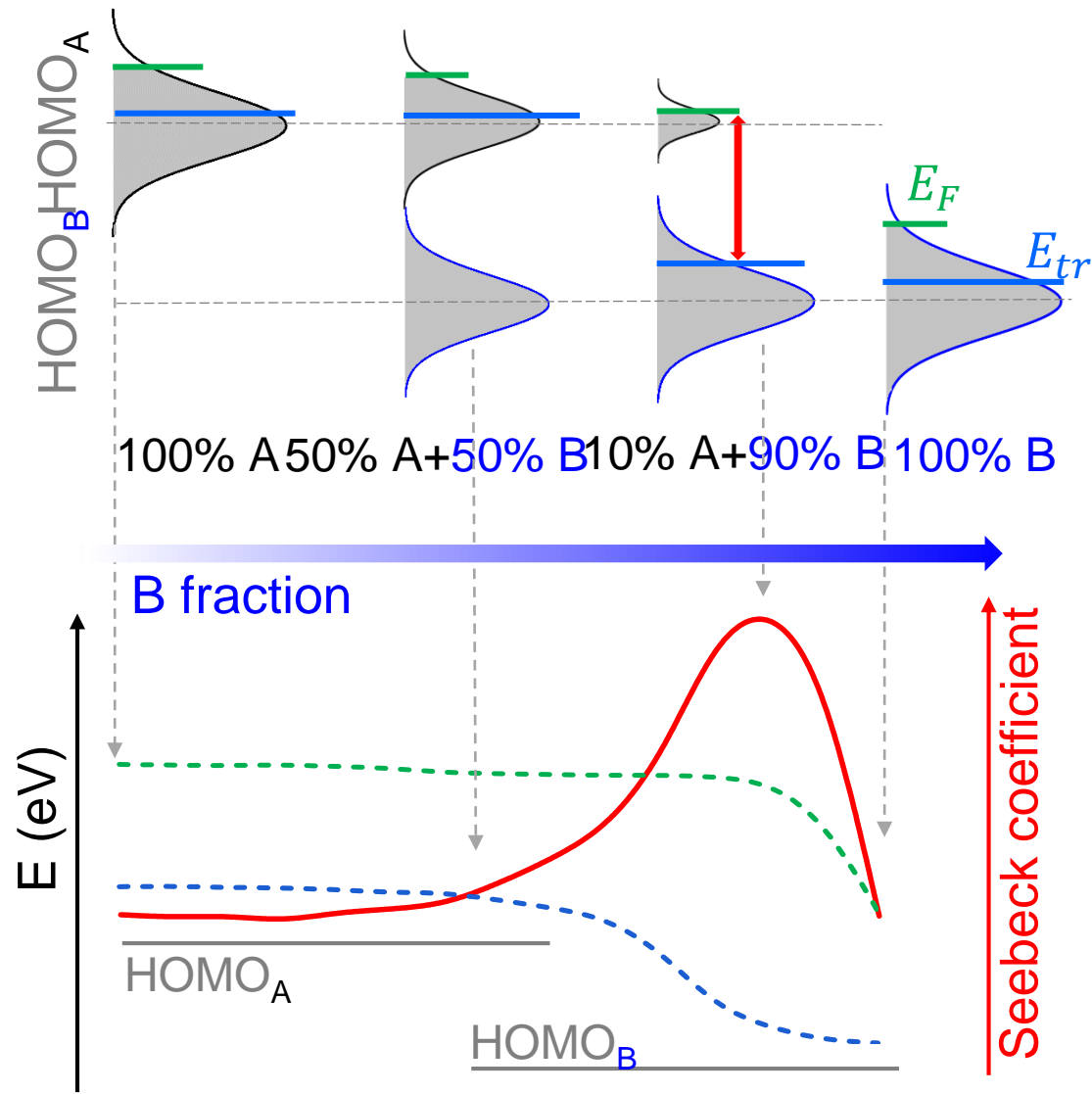
UPS by Xianjie Liu & Mats Fahlman, LiU
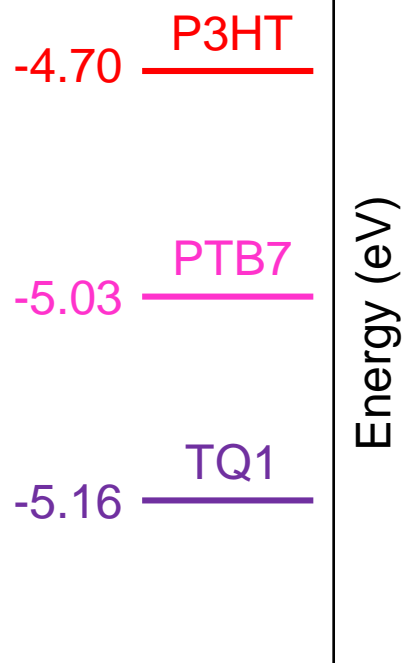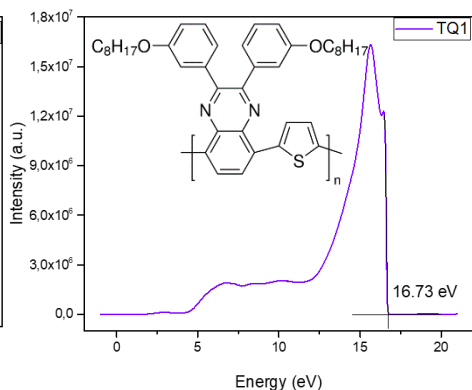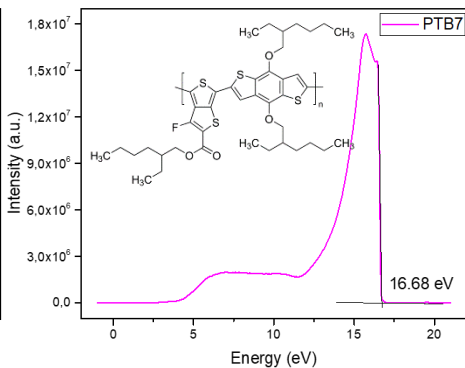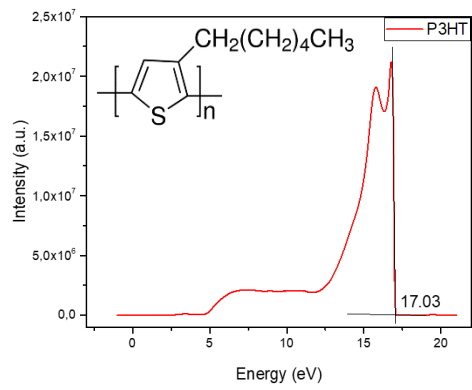
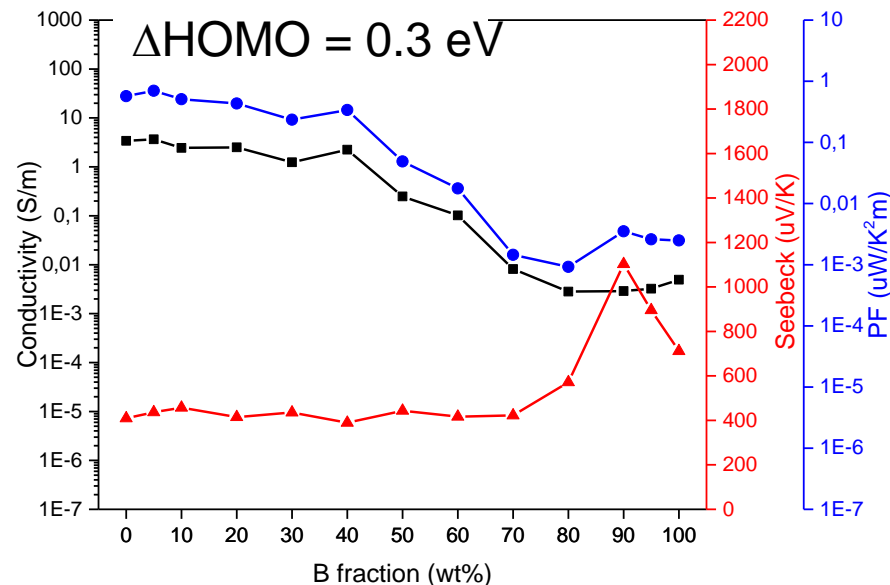| CPs	E_F (eV)	IP (eV)
P3HT	4.19	4.7
PTB7	4.54	5.03
TQ1	4.49	5.16

dopant: F_4TCNQ
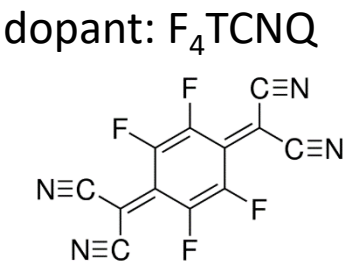
Experiments:

Concept:
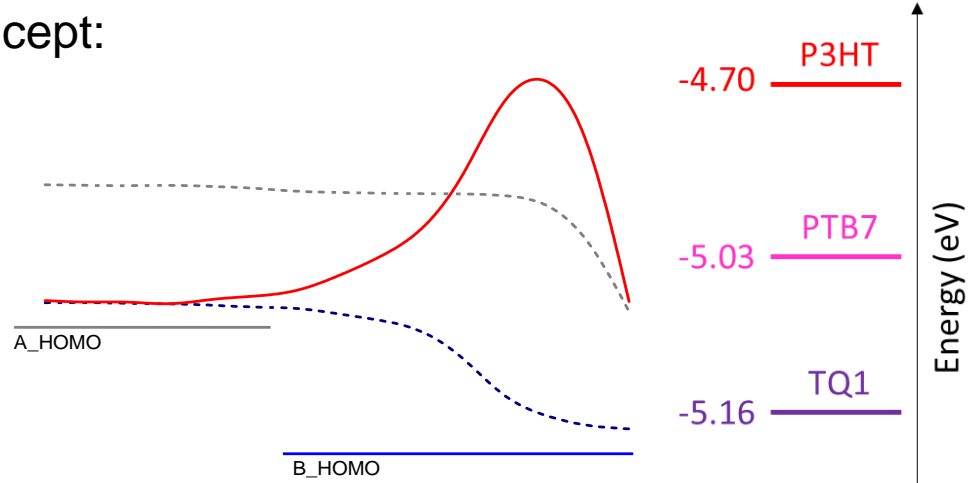
- High electronic Seebeck coefficients of 1-2 mV/K
- Cannot be explained by effective medium model

Simulations by kinetic Monte Carlo:


ΔHOMO = 0.3 eV

ΔHOMO = 0.5 eV
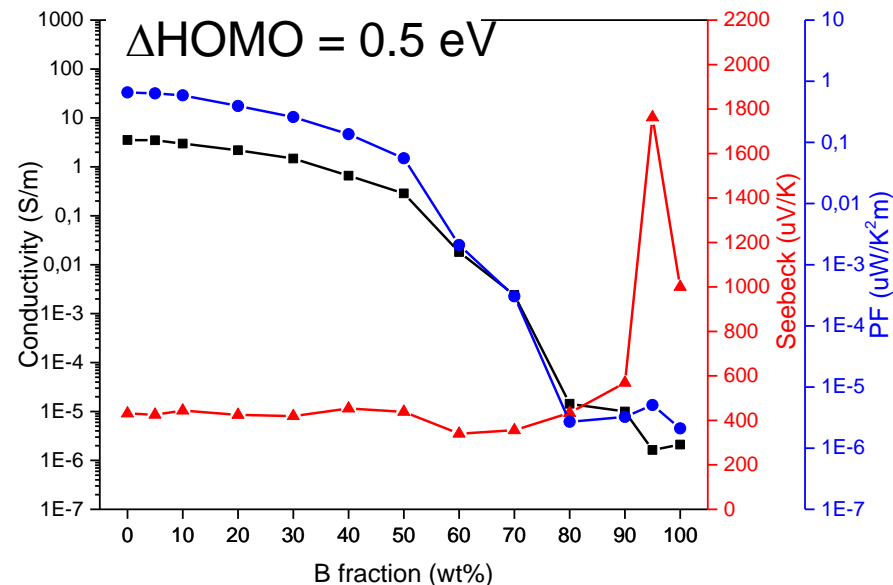
- Reproduces experimental findings
- No free fitting parameters involved

doping concentration $c = 10^{-2}$
attempt to hop frequency $v_0 = 10^{-13}$ s^{-1}
intersite distance $a_{NN} = 1.8$ nm
Gaussian disorder $\sigma_{DOS} = 0.075$ eV
temperature $T = 300$ K
HOMO$_A$ - LUMO$_{dopant}$ = 0.24 eV
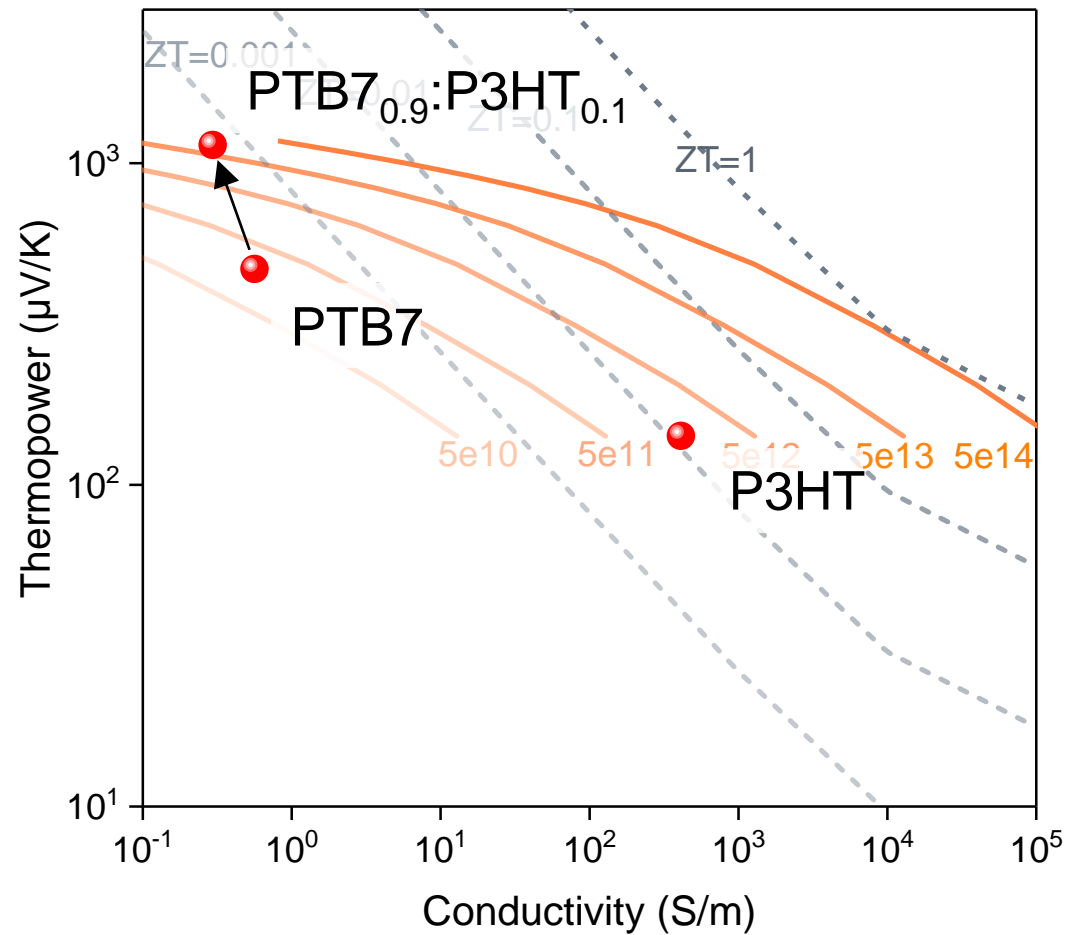
DOS engineering can be used to improve ZT by selectively increasing S.

Future: with a better starting material…

morphologies changed by DIO

pristine

5% DIO
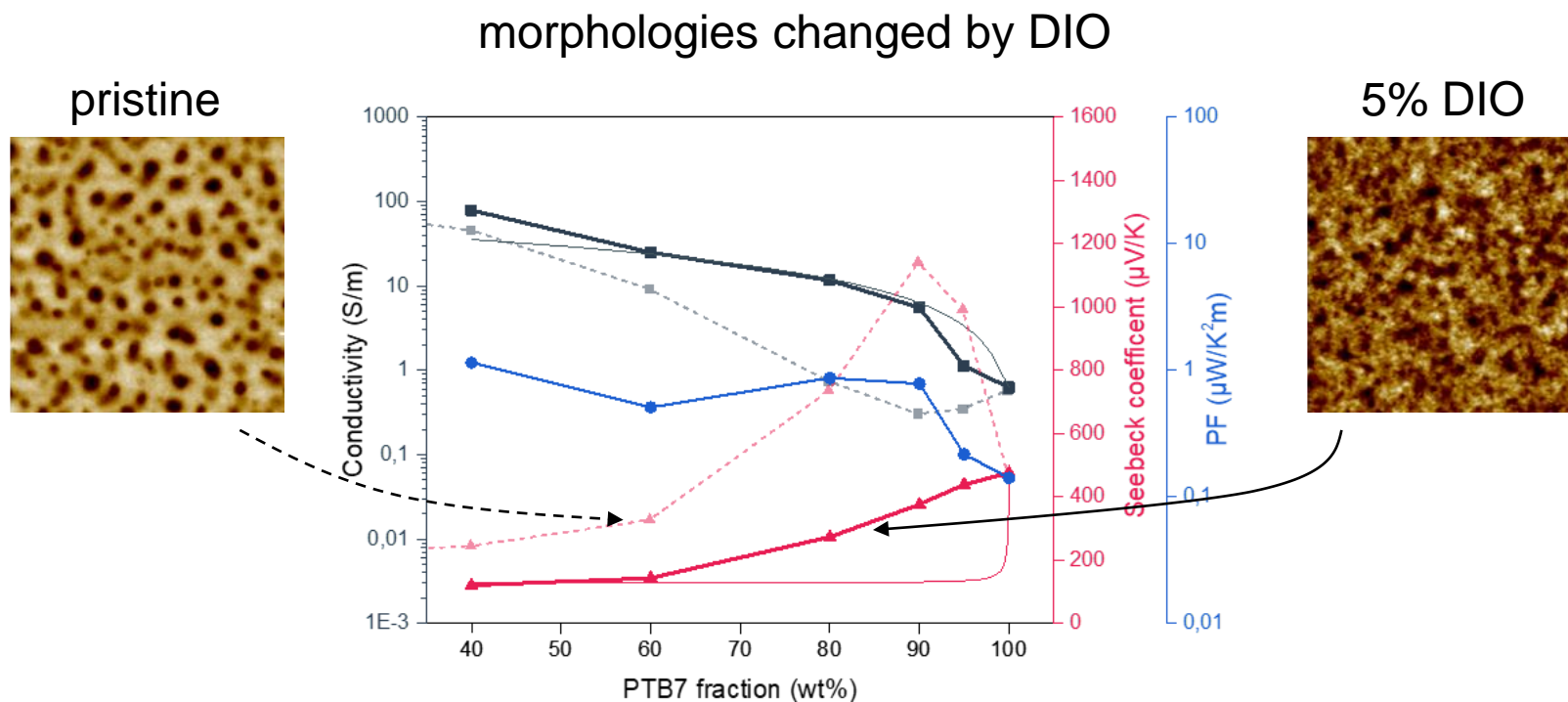
high thermopower in blend systems depends on energy levels
and phase separation....

- **Unintentional DOS design** in doped organic semiconductors leads to 'universal' power law relation between S and σ.

- n- and p-type materials follow same trend

- n-type materials have higher σ at equal S

- **Intentional DOS design** gives S = 1-2 mV/K at reasonable σ

- Method is demonstrated for n- and p-type blends (but morphology matters)

- Experiments are quantitatively reproduced by numerical simulations

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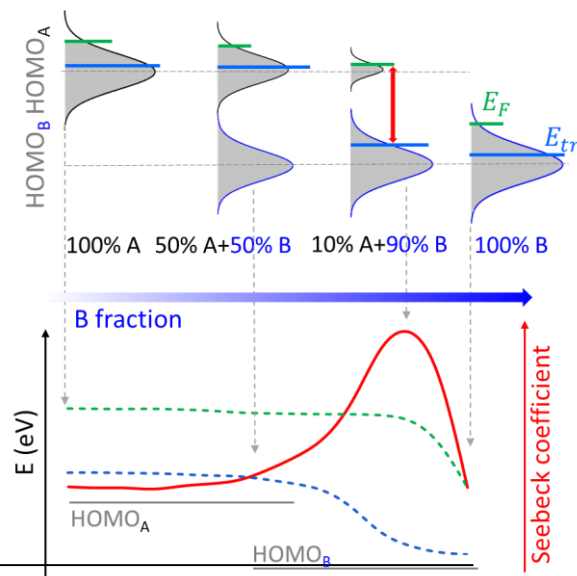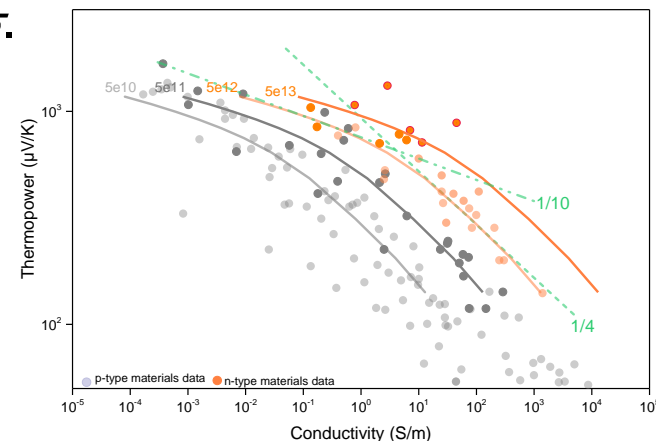
Many thanks to…

Guangzheng Zuo

Hassan Abdalla

Olof Andersson

Xianjie Liu

Mats Fahlman

Zhaojun Li

Ergang Wang

& Thanks for your attention!

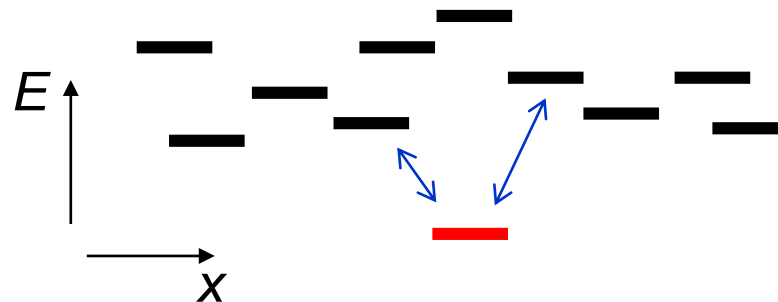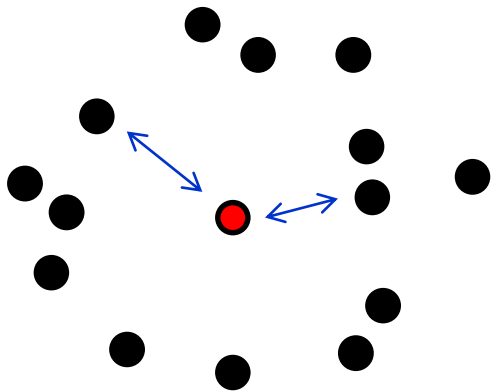LINKÖPING UNIVERSITY

FAQ: It may seem odd that more attention is paid to energetic disorder than to spatial disorder. Why?

Answer: Consider a 'bad site' in real space and in energy space:

$$\nu_{ij} \propto \exp(-2\alpha r_{ij})$$

$$\nu_{ij} \propto \exp\left(-\frac{E_j - E_i}{k_B T}\right) \quad \text{if } E_j - E_i > 0$$

$$\nu_{ij} = \text{const} \qquad\qquad \text{if } E_j - E_i < 0$$

The tunneling rate is symmetric, so a spatially bad site is hard to get in, and will hardly contribute. Thermal activation is asymmetric, so an energetically bad site is easy to get in and hard to get out.

idea for this slide: Sergey Novikov