6.4 Disorder-Controlled Transport

Criteria for Polaronic Transport and Disorder-Controlled Transport

- incoherent transport prevails if any energy present due to dynamic disorder and/or static disorder is larger than the interaction energy between neighboring sites

$$H_1 \ll H_2, H_3, H_4, H_5$$

- charge carriers become localized at individual sites and proceed by a sequence of non-coherent transfer events
- polaronic transport if dynamic disorder dominates in an otherwise perfectly ordered crystal

$$H_1 \ll H_2, H_3, \quad H_4 = H_5 = 0$$

- charges form polarons and transport takes place via thermal activated inter-site hopping
- disorder-controlled if static disorder dominates in non-crystalline systems

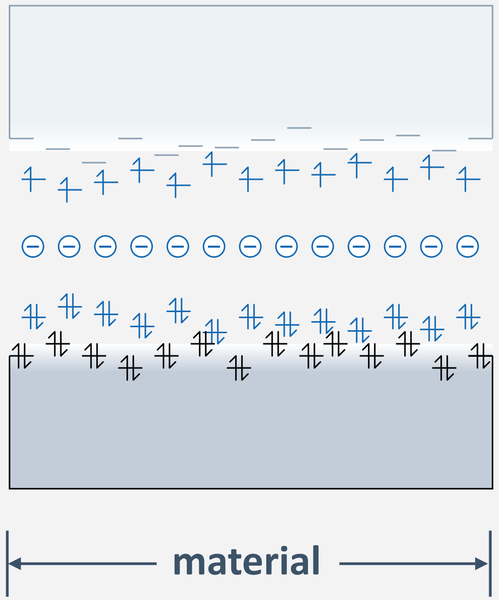
$$H_1 \ll H_4, H_5, \quad H_2 = H_3 = 0$$

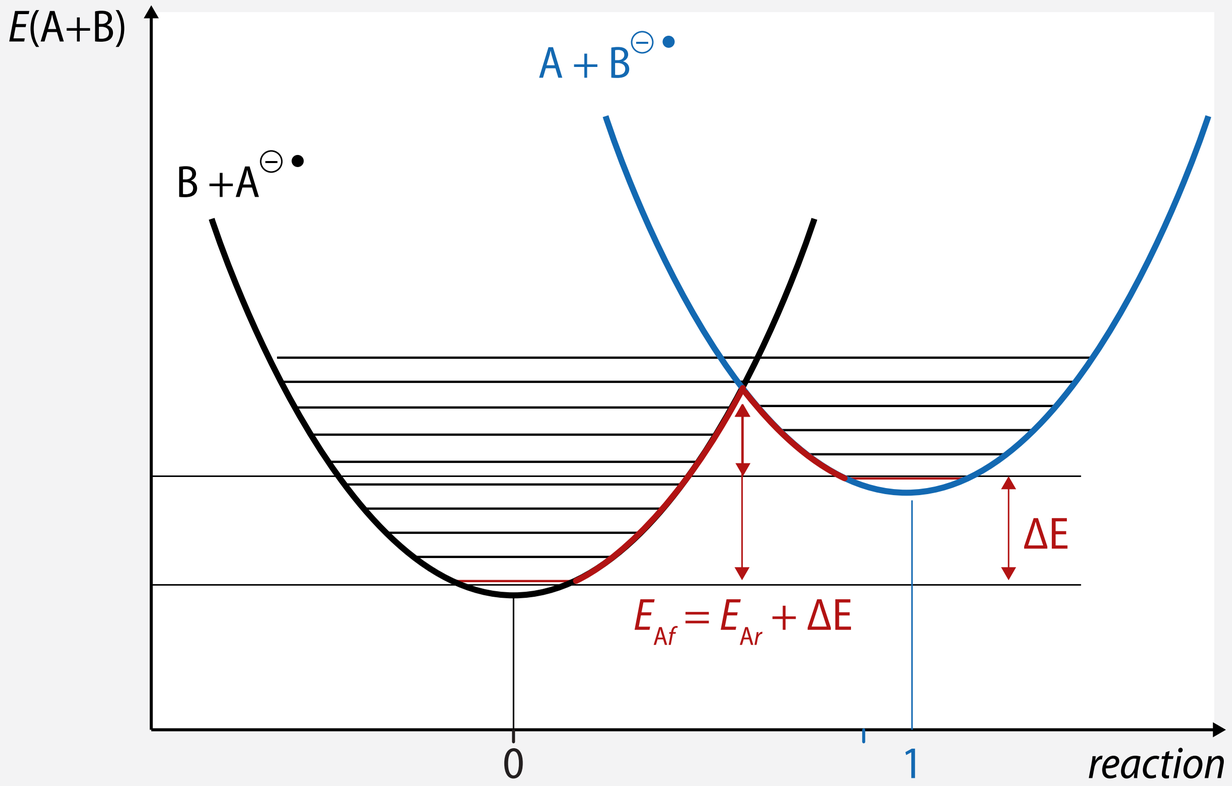
- transport is random walk by “hopping” between neighboring sites with different energies

KEY CONCEPT: see A. Köhler and H. Bässler, Electronic Processes in Organic Semiconductors, p. 217-233

Charge Transfer from One Molecule to a Neighbor

- energy sites are neither equidistant, nor isoenergetic, nor equally coupled
- transport steps become unsymmetric





- **charge transport takes place by an incoherent sequence of charge transfer events**
- **transport according to random walk determined by energy landscape (and electric field)**

Gaussian Disorder Model (Bässler Disorder Model)

- transport according to random walk determined by occupational probability p_i at site i

$$\frac{dp_i}{dt} = \sum_{i \neq j} \left\{ -w_{ij}\ p_i\ [1 - p_j] + w_{ji}\ p_j\ [1 - p_i] - \Lambda p_i \right\} \quad \text{with losses } \Lambda$$

- for low charge carrier density: $p_i\, p_j = 0$

$$\frac{dp_i}{dt} = \sum_{i \neq j} \left\{ -w_{ij}\ p_i + w_{ji}\ p_j - \Lambda p_i \right\}$$

- **Gaussian Disorder Model (GDM) assumes Gaussian distribution of site energies due to large number of randomized Van der Waals couplings between neighboring sites**

$$g(\varepsilon) = \frac{1}{\sqrt{2\pi}\ \sigma}\ e^{-\frac{(\varepsilon - \varepsilon_0)^2}{2\sigma^2}} \quad \text{with standard deviation / disorder parameter } \sigma$$

- Correlated Disorder Model (CDM) assumes correlation between site energies and Van der Waals couplings to neighboring sites

Microscopic View of Disorder-Controlled Charge Transport

- **each transfer step becomes asymmetric depending on whether $\Delta E < 0$ or not**

$$w_{ij} = \nu_0 \quad e^{-2\gamma\, r_{ij}} \qquad \text{for} \quad \varepsilon_j \leq \varepsilon_i$$

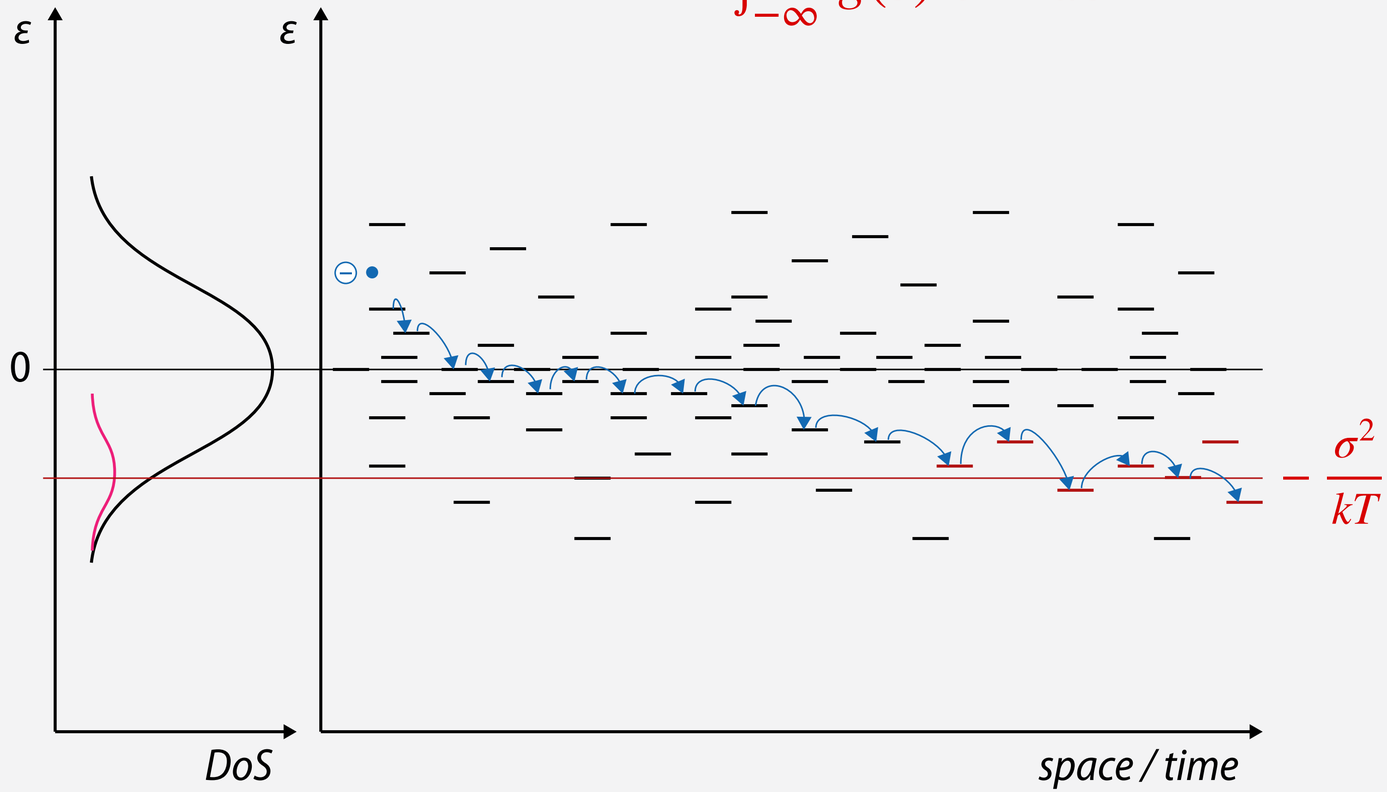
$$w_{ij} = \nu_0 \quad e^{-2\gamma\, r_{ij}} \; e^{-\frac{(\varepsilon_j - \varepsilon_i)^2}{k_\mathrm{B} T}} \qquad \text{for} \quad \varepsilon_j \geq \varepsilon_i$$

  - frequency factor ν_0 describes the base frequency of vibrational transfer (attempts to hop)
  - distance-dependent term (hopping distance r_{ij} and inverse electron localization radius γ)
  - Boltzmann factor describes the temperature dependence of *endergonic* steps

Temperature Dependence of Disorder-Controlled Transport

- mean quasi-equilibrium energy of the charge carriers is (variance σ of the Gaussian distribution

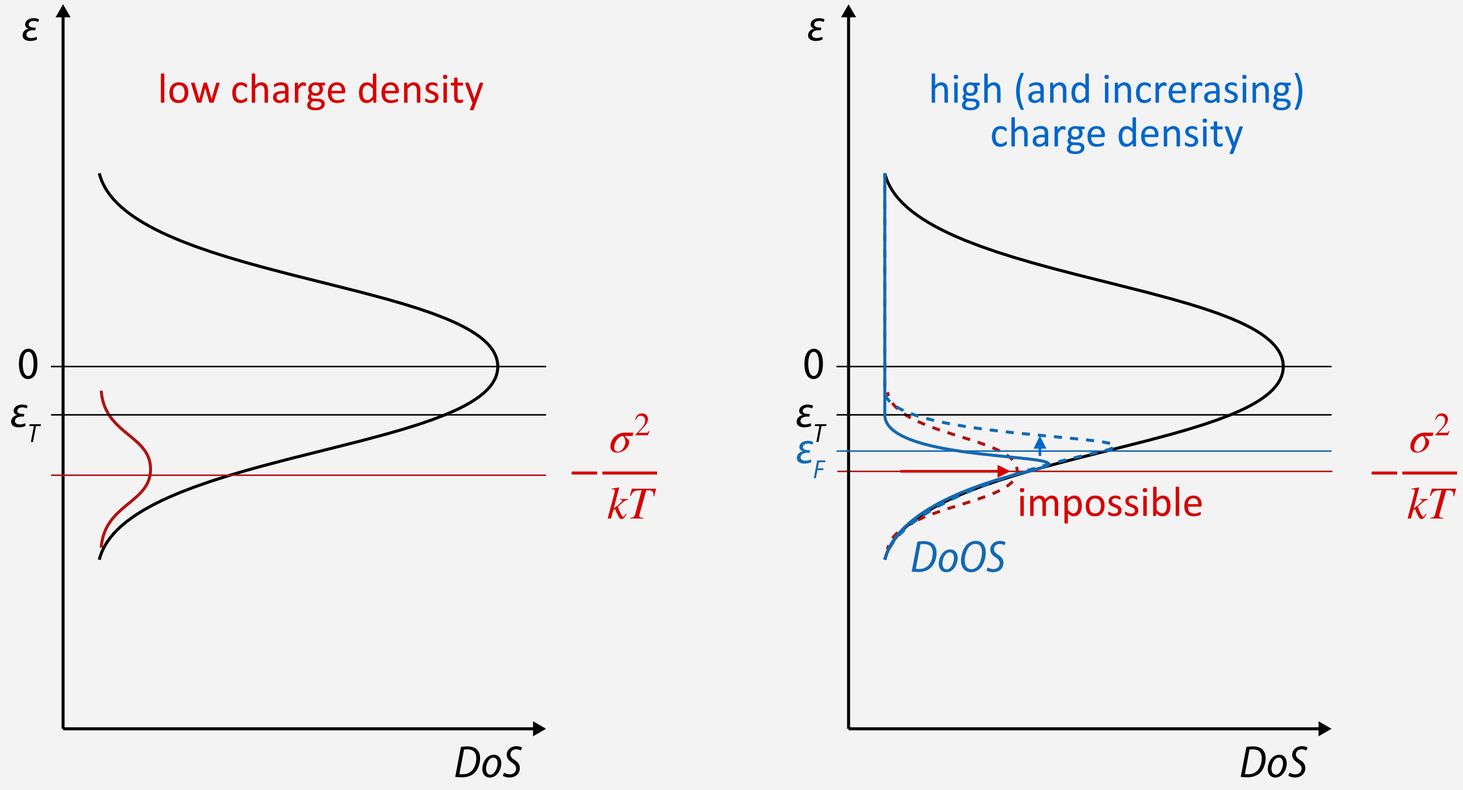
$$\varepsilon_\infty = \lim_{t\to\infty} \varepsilon = \frac{\int_{-\infty}^{+\infty} \varepsilon\ g(\varepsilon)\ e^{-\frac{\varepsilon}{kT}} d\varepsilon}{\int_{-\infty}^{+\infty} g(\varepsilon)\ e^{-\frac{\varepsilon}{kT}} d\varepsilon} = -\frac{\sigma^2}{kT}$$



- **therefore, the temperature dependence does not show Arrhenius behavior but** $\mu = \mu_0\ \ e^{-\left(\frac{\sigma}{kT}\right)^2}$

Transport at High Charge Densities

- at high charge carrier densities, lowest energy trap states become “filled”
- Boltzmann statistics become Fermi Dirac statistics (Pauli principle)



- **density of occupied states with (temperature-independent) pseudo-Fermi level**
- **lower activation energy, further decreasing with charge density, and Arrhenius behavior**

Superposition of Static and Dynamic Disorder

- **complete view of dynamic disorder, static disorder and effect of the electric field**

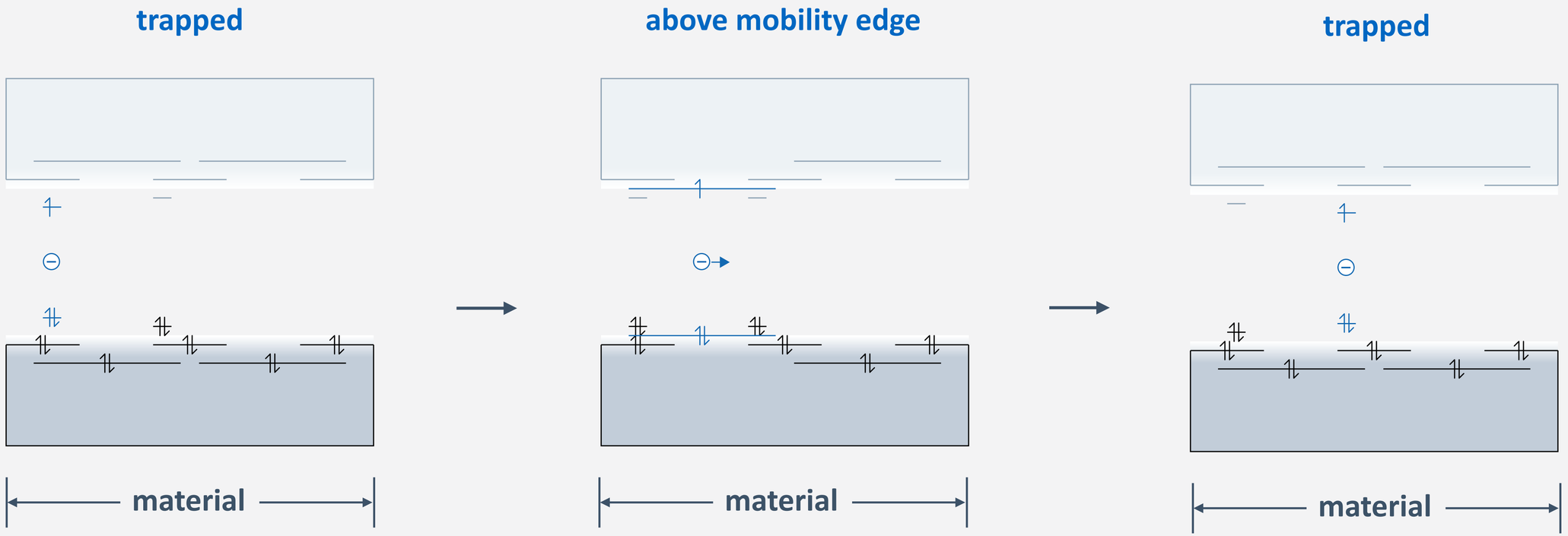
$$\mu = \mu_0 \; e^{-\frac{E_A}{kT}} \; e^{-C_1\left(\frac{\sigma}{kT}\right)^2} \; e^{-C_2\sqrt{\frac{F}{\sigma}}}$$

  - hence switch from disorder-controlled to polaronic transport at a critical temperature T_C

$$T_C = C_1 \frac{\sigma^2}{kE_A} \quad \text{with geometric factor } C_1 = \left(\frac{2}{3}\right)^2 \approx 0.44$$

Multiple Trap and Release (MTR) Model

- “band edge disorder” model assumes disorder, distribution of states near band edge
- states located within bands more extended, states at band edge more localized traps

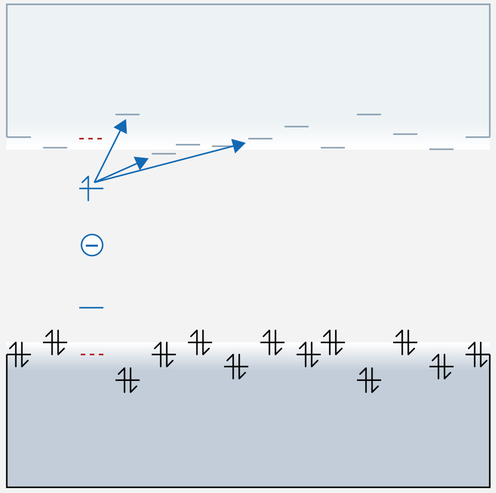


- **charges temporarily trapped in localized states, but no “deep traps” if disorder not too large**
- **promotion of charge into more extended state “above mobility edge”, drift in electric field**
- **subsequent “retrapping” into more localized “resting state”**

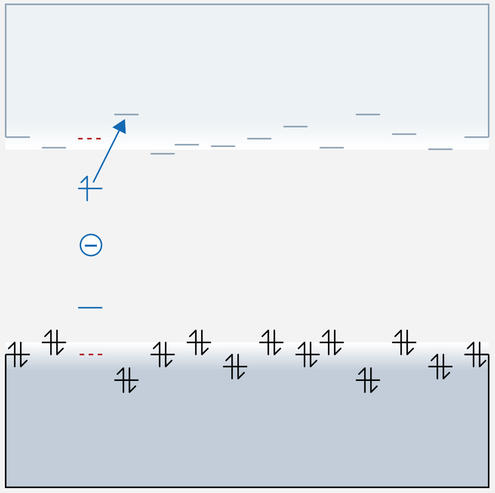
Variable Range Hopping (VRH) and Nearest Neighbor Hopping (NNH)

- variable range hopping for less disordered systems or at higher temperatures ($\Delta E \approx k_B T$)
- variable range hopping abundant in literature, but lacks physical basis

variable range hopping (VRH)



nearest neighbor hopping (NNH)



Mott's law $k_{\mathrm{VRH}} = C_{\mathrm{VRH}} \cdot e^{-(T_0/T)^{1/4}}$

- **nearest neighbor hopping in highly disordered systems, or at low temperatures ($\Delta E \gg k_B T$)**