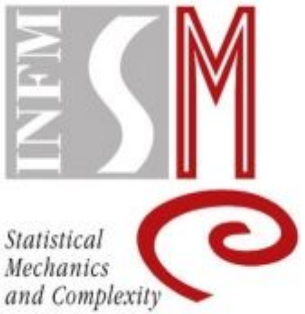
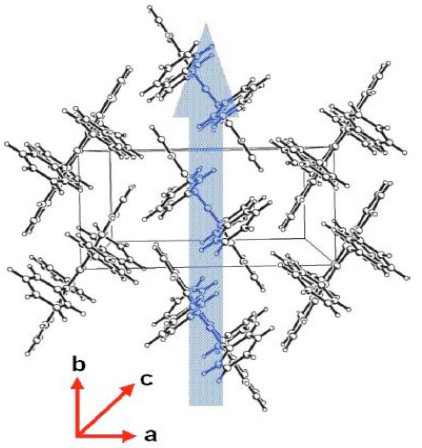
Band motion and incoherent diffusion in organic molecular semiconductors: two sides of the same coin

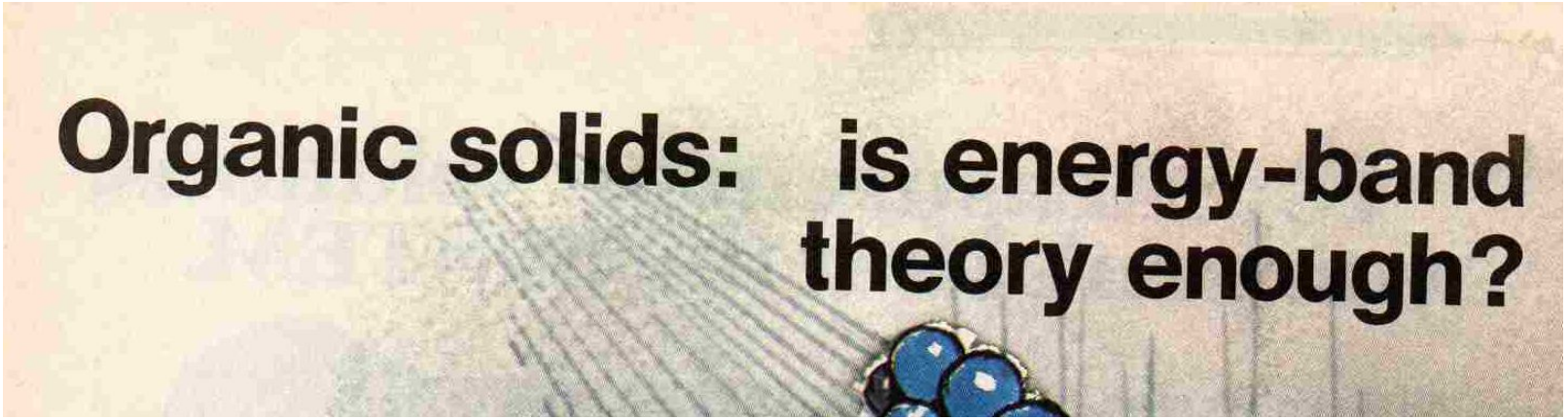
S. Fratini (Grenoble), S. Ciuchi (l'Aquila)



Outline



- Organic molecular crystals
- Transport theory, why interesting?
  Duality band-like vs localized not solved yet
- Strategy: study a simple model and extract the complex physics
  - Excitation spectrum (localized+Bloch states)
  - Consequences on transport → crossover regime



Chemist's view... real space
Electrons hop from molecule to molecule

[Duke & Schein, Physics Today 1980]

The molecular property

As we mentioned earlier, a pre-eminent feature of the organic solid state is the persistence of molecular identity.

for solid-state physicists. But perhaps their most interesting aspect, however, is the persistent challenge that organic crystals afford to conventional theories of transport in solids. After over two decades of intensive investigation, the temperature and field dependence of the mobilities of charge carriers in van der Waals crystals remain unexplained by extant models of either band or hopping transport. Thus, organic materials con-

Physicist's view... momentum space
Electrons form weakly scattered Bloch states

served behavior. Hence, Bloch-type states *do* appear to occur in some molecular crystals in certain temperature ranges. Above 100 K in naphthalene, however, another mechanism appears to limit the mobility. The usual alternative to transport via Bloch-type states is the hopping of localized carriers. It would

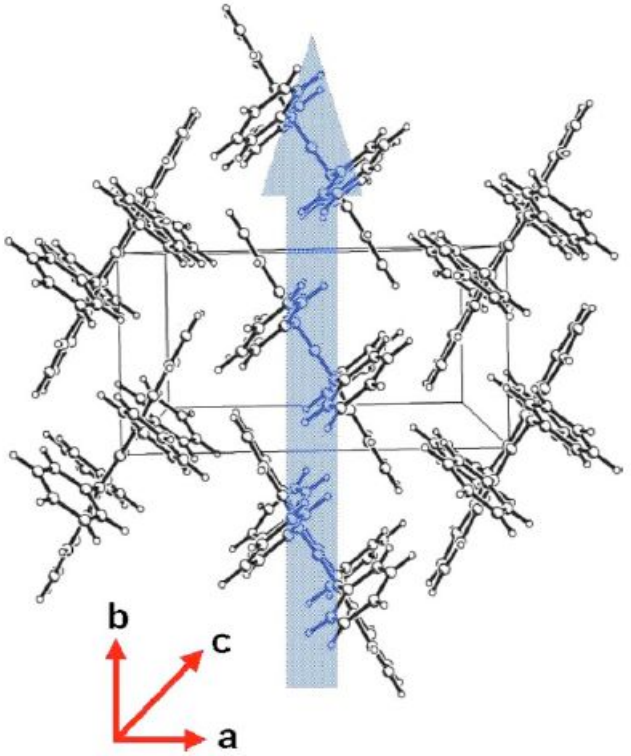
« one of the major outstanding mysteries in solid-state physics »
→ the problem is still open

Can we reconcile these two points of view?

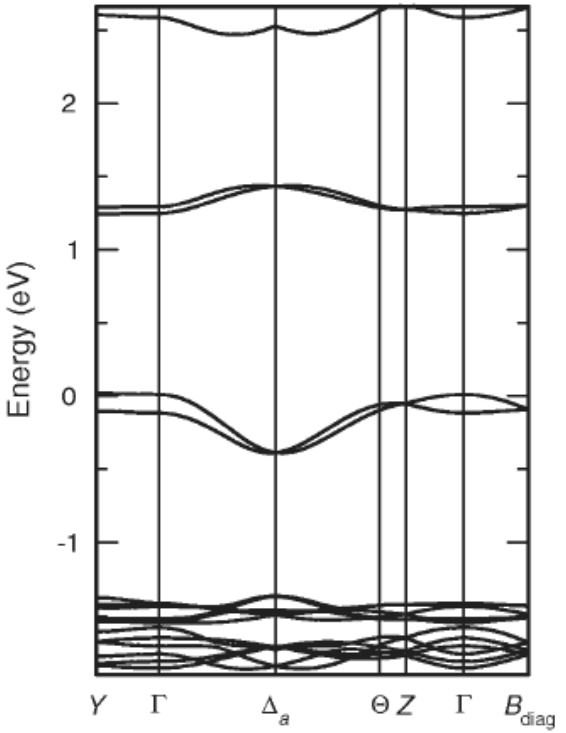
Band structure

- VdW bonding, a=4-8A, « persistence of molecular identity »
- Low overlap integrals → narrow bands W~0.1-0.4eV

  Tendency to localization, polarons, breakdown of band picture?



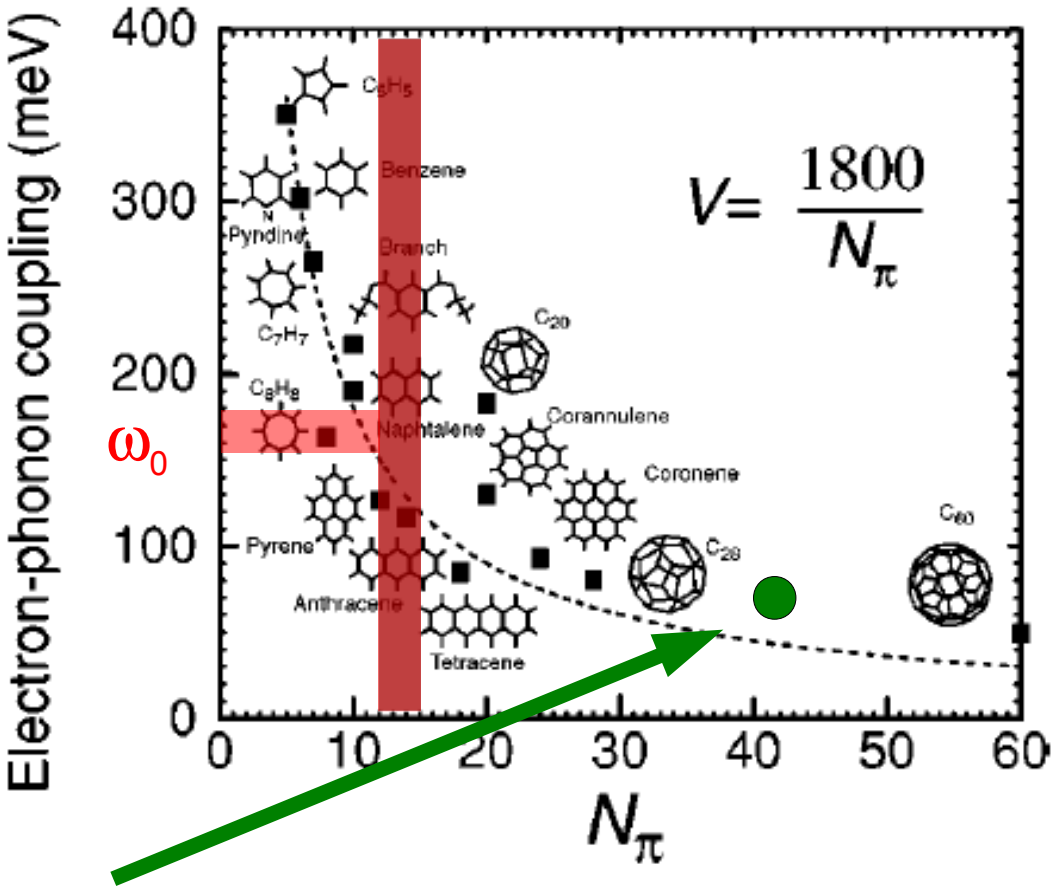
Herringbone struct



Rubrene, [DaSilva AdvMat05]

Intra-molecular el-ph coupling (larger molecules, better conductors)

Strong coupling (polaronic) ↔ weak coupling



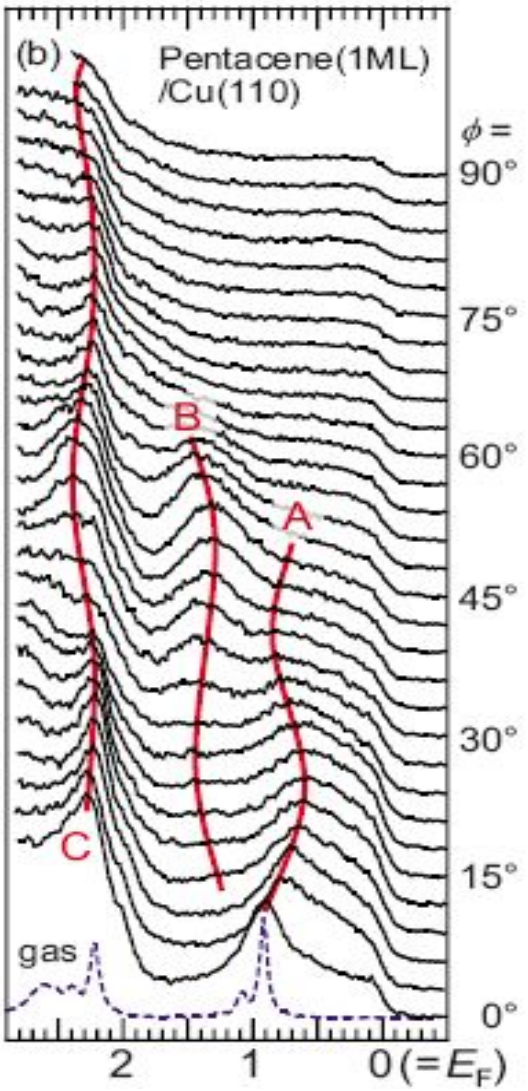
[Devos Lannoo PRB98]
[Coropceanu PRL02]

Polarons if
$E_P/\omega_0 > 1$ → phonon cloud

[Troisi AdvMat07] → Rubrene = 79meV but ω_0=173 meV → weak coupling

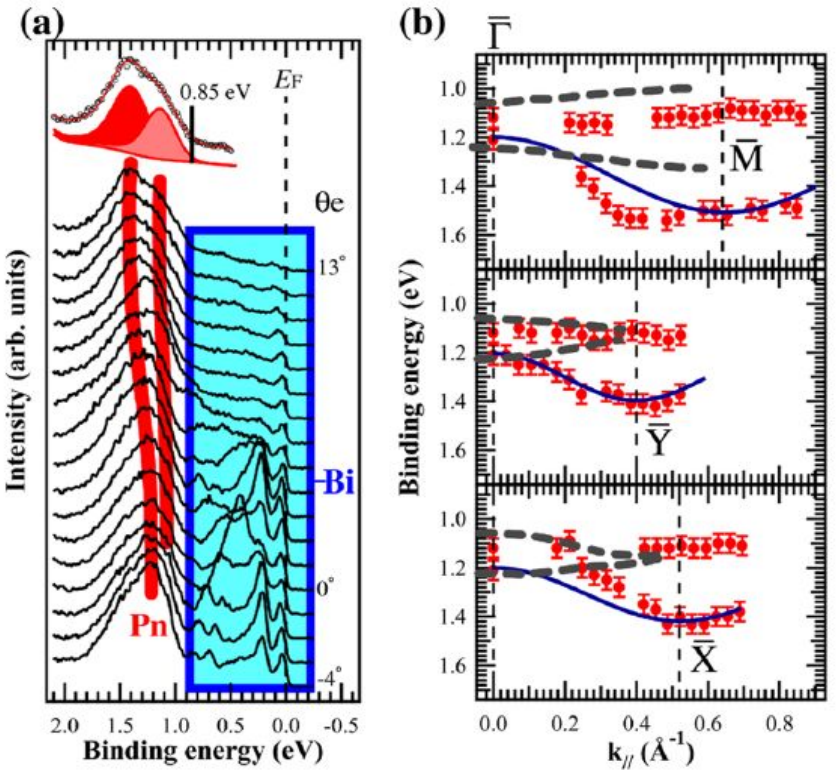
inter-molecular coupling is 24meV with ω_0=6meV → larger effect on transport

Photoemission



Pentacene [Kakuta PRL07, Yamane PRB07]:

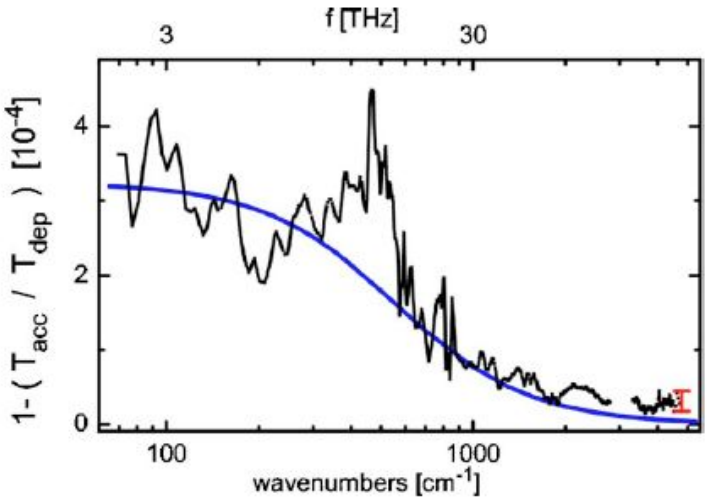
- similar to gas phase
- electronic bands are seen in 1ML films
- broadening~bandwidth (intrinsic+substrate)



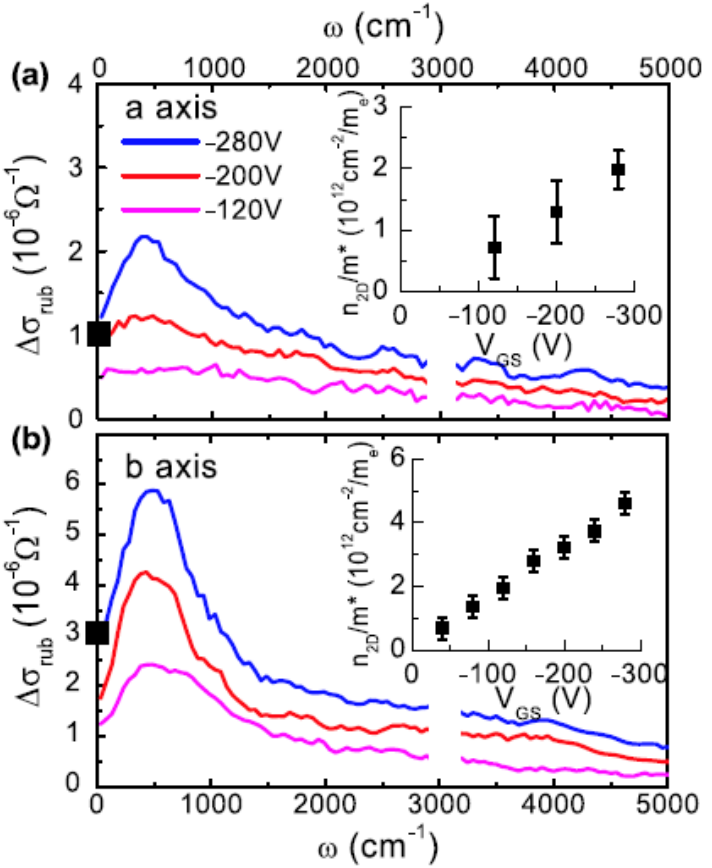
Optical absorption

Light Quasiparticles Dominate Electronic Transport in Molecular Crystal Field-Effect Transistors

Z. Q. Li,[1,*] V. Podzorov,[2] N. Sai,[1,3] M. C. Martin,[4] M. E. Gershenson,[2] M. Di Ventra,[1] and D. N. Basov[1]



Rubrene [Fischer APL06]

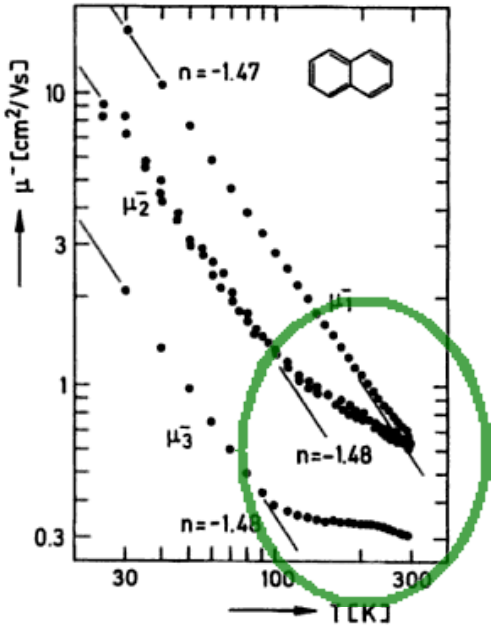


Rubrene [Li PRL07]

- «Drude-like» absorption (too broad?)
- Low-frequency maximum (?)
- m*~1-2 from sum-rule analysis, anisotropy agrees with band struct.

mobility (TOF, FET)

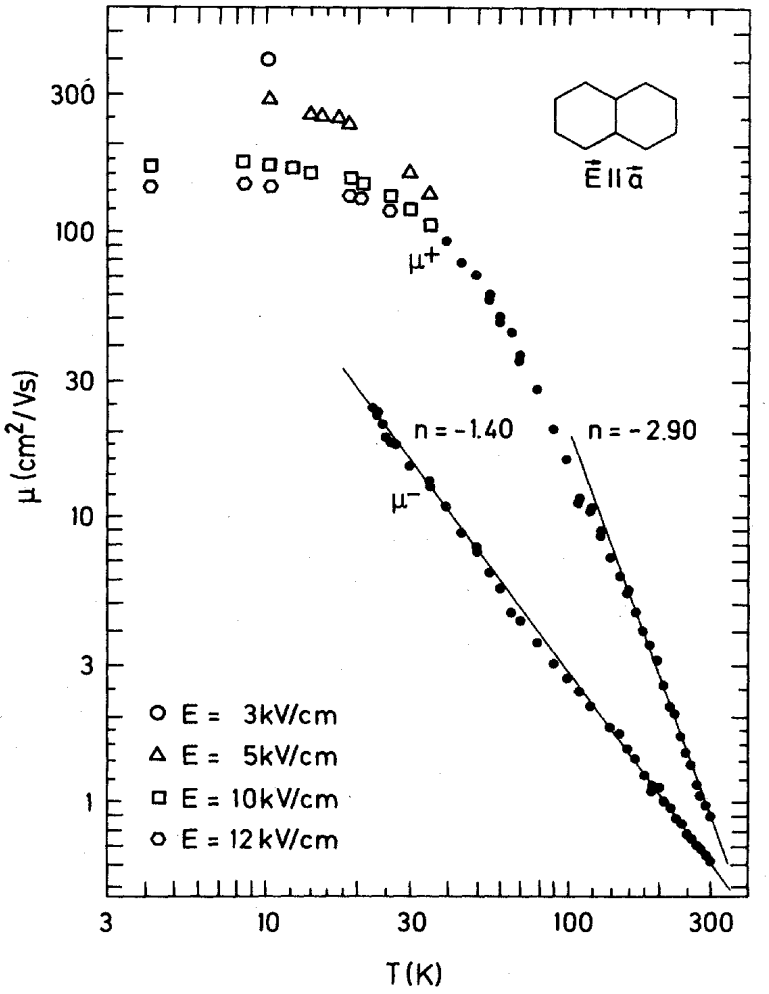
- band-like, T^{-n} with n=0.5-3
- very low values μ=0.1-400 cm^2/Vs (graphene >10^5, 2DEG >10^7)
- $\mu_{holes} > \mu_{electrons}$
- anisotropy (~band structure)



?

naphthalene

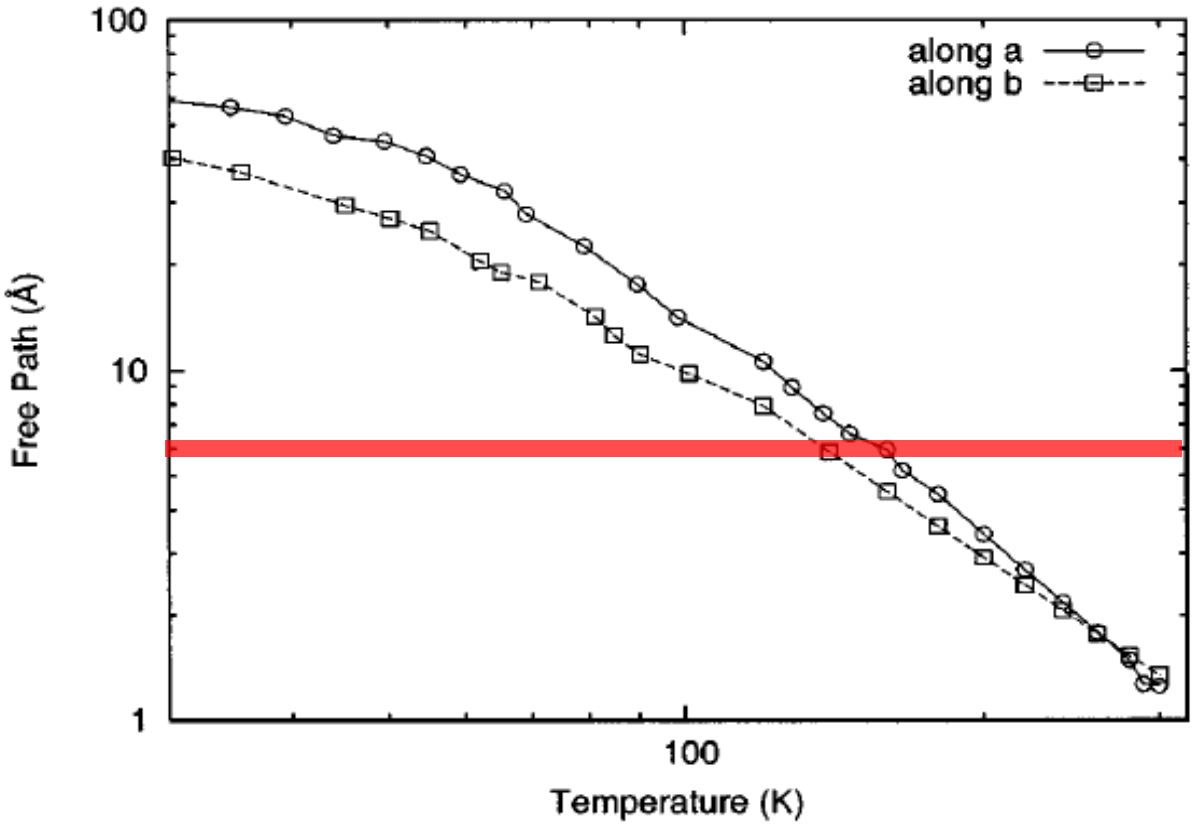
[Karl SynthMet 03]



Long-standing problem: mean-free-path

Several experiments indicate that k-space description is not completely inadequate, but...

How can μ be « band-like » and $l_{\mathrm{mfp}} < a$?

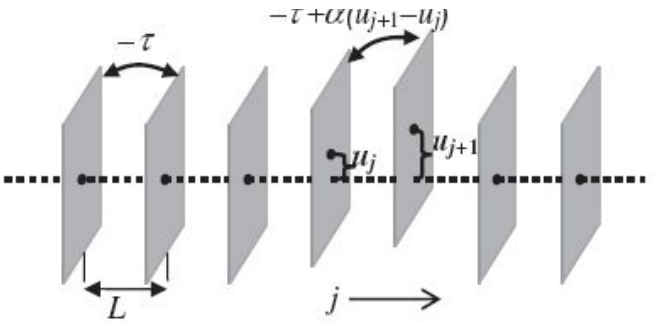


$l_{\mathrm{mfp}} \sim a$

Extractred from hole mobility in naphthalene via band-structure calculations [Cheng JCP03]

Model for organic semiconductors (paradigmatic)

$$H = -t \sum_{<ij>} \left[1 - \sqrt{2\lambda}(X_i - X_j)\right] c_i^+ c_j + \frac{1}{2} \sum_i M\omega_0 X_i^2$$



[Duke & Schein, Physics Today 1980]
[Munn & Silbey JCP85]
[Hannewald & Bobbert PRB04]
[Troisi PRL06]

- molecular nature, narrow bands → tight binding t~ 50-100 meV
- mechanical softness, large thermal fluctuations of the lattice
  - Optical mode ω_0~5-10 meV, modulates transfer integral
  - Inter-molecular coupling λ~0.05–0.2
- Neglect intra-molecular (local) coupling, restrict to 1D

Boltzmann (band) theory

[Glarum JPCS63, Friedman PR65]

- Semi-classical: electron loses its coherence between successive scattering events

$$\mu = (e/k_B T)\langle v_x^2 \tau \rangle$$

Statistical average

$$\langle \ldots \rangle = \sum_k e^{-\varepsilon_k/T} \ldots$$

relaxation time

- T<2t, usual limit (model,d-dependent)

$$\mu = \mu_0 \frac{1}{4\sqrt{\pi}\lambda} \left(\frac{t}{T}\right)^{3/2}$$

- T>2t, high temperature limit (universal)

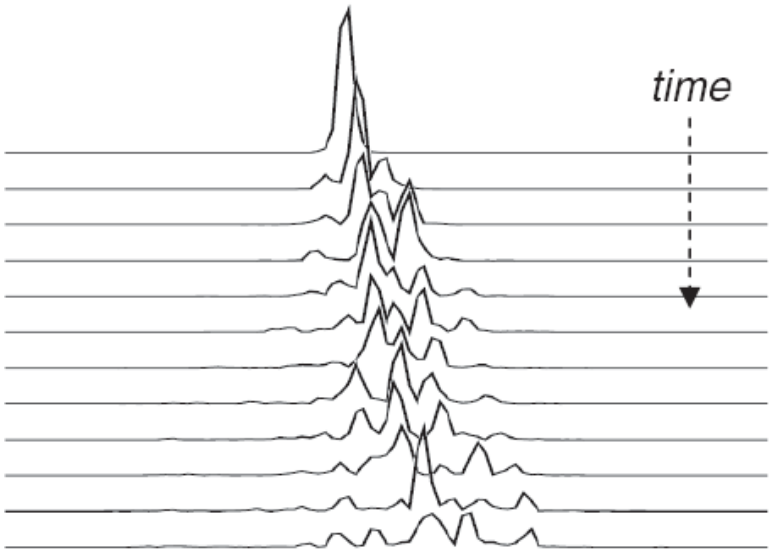
$$\mu = \mu_0 \frac{1}{2\pi\lambda} \left(\frac{t}{T}\right)^{2}$$

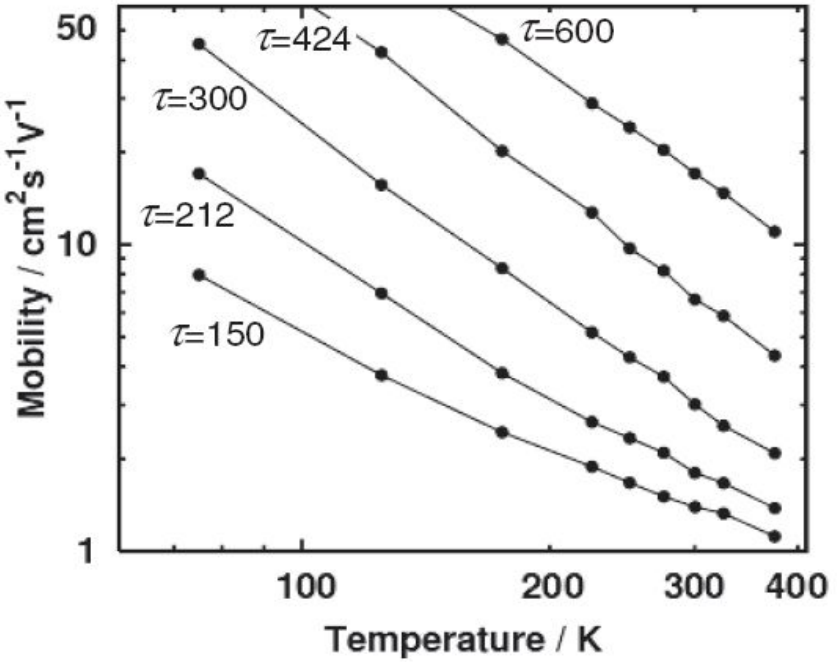
- Power-law decrease with T
- $\mu > \mu_0$ for band conduction (qualitative argument)

$$\mu_0 = \frac{ea^2}{\hbar} = 7 cm^2/Vs \quad (a = 7\mathring{A})$$

Quantum-classical simulation

- Classical harmonic oscillators/ quantum electrons [Troisi PRL06]





- Electron wavepacket looks localized on few lattice sites
  → « riding the lattice waves »
- still $\mu \sim 1/T^2$ is Boltzmann-like at low T, low λ
  (with exponent appropriate to T>2t~400-1600K, how can it be?)
- Alternative calculation (acoustic phonons) yields $\mu \sim 1/T^{1.7}$ [Picon PRB07]

Our approach: understand transport from spectral properties

- Classical phonons, $T>\omega_0$
- thermal lattice disorder (variance ~kT)

  → MonteCarlo method for the Green's function

$$G(\omega, i, j, X) = < j | \frac{1}{\omega - H_{el}(X)} | i >$$

  - Up to 2^{16} sites, algorithm for G_{ij} based on regularization of recursion formulas, no ED needed
  - Finite size effects controlled by attaching 2 leads

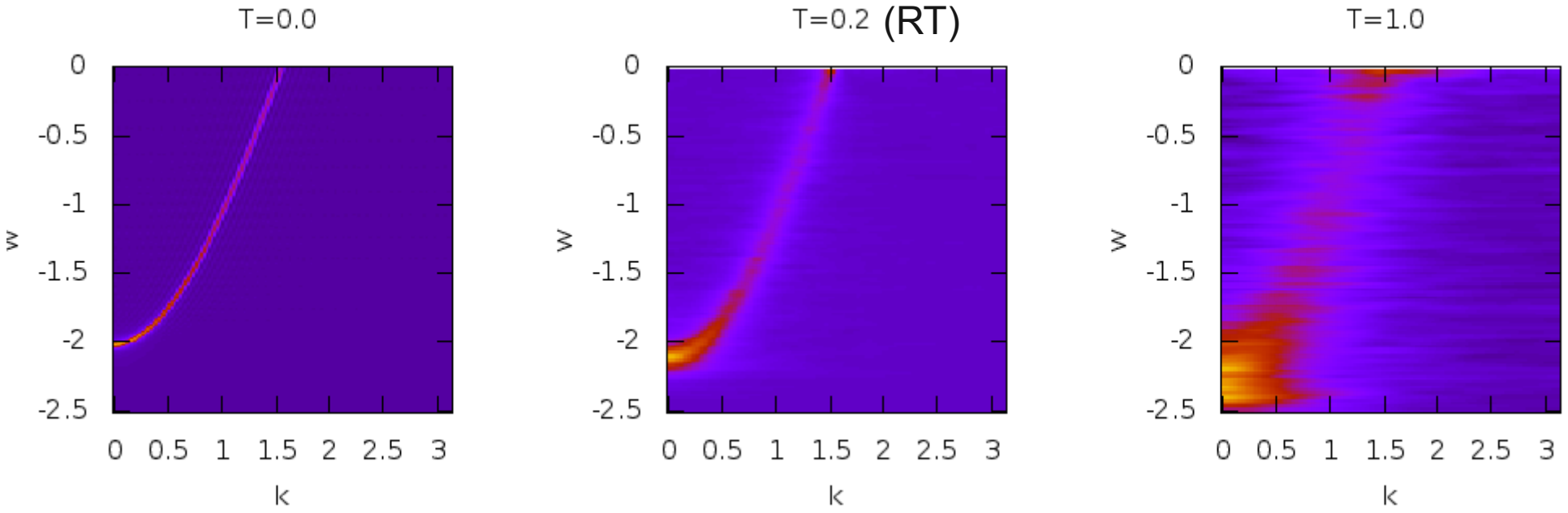
- Green's function

  → Exact one-particle excitation spectrum

  → momentum/energy/spatially resolved properties
- Mobility → Kubo formula without vertex corrections (almost exact...)

Spectral function A(k,ω)

$\lambda = 0.17$

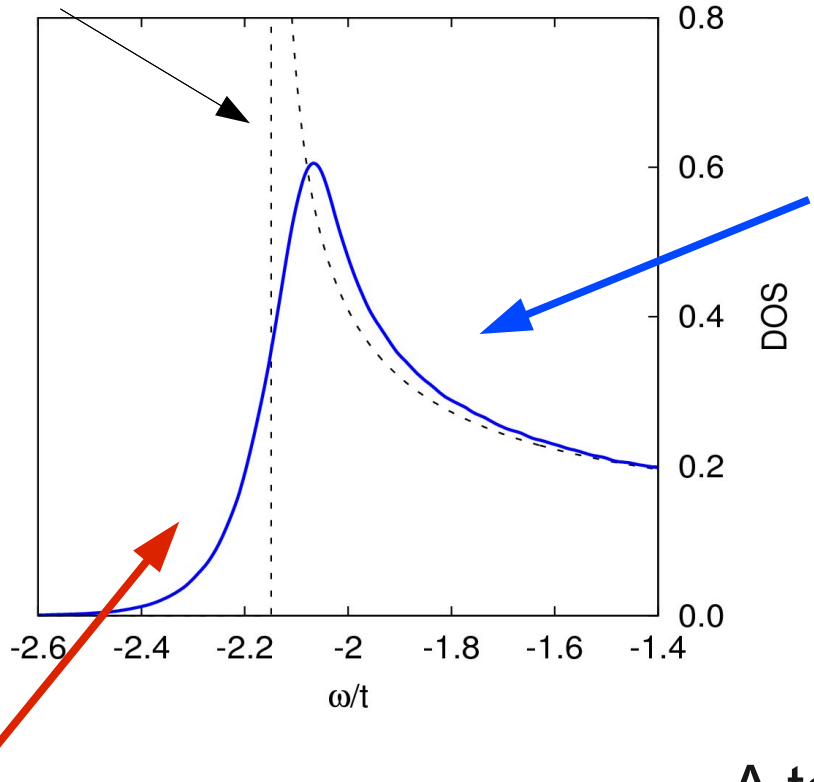


s/t=0 s/t=0.5 s/t=1.2

- k-states are well defined at moderate thermal disorder (rubrene, ~RT)
- low-k states are partially protected by off-diagonal coupling
- broadening $s = t\sqrt{8\lambda(T/t)}$
- breakdown of qp picture when $l_{\mathrm{mfp}} < a \quad (s > t)$
- otherwise, ARPES dominated by the band nature of carriers

Density of states (k-integrated, local)

Free 1D DOS



$$\rho(\omega) = \sum_k A(k,\omega)$$

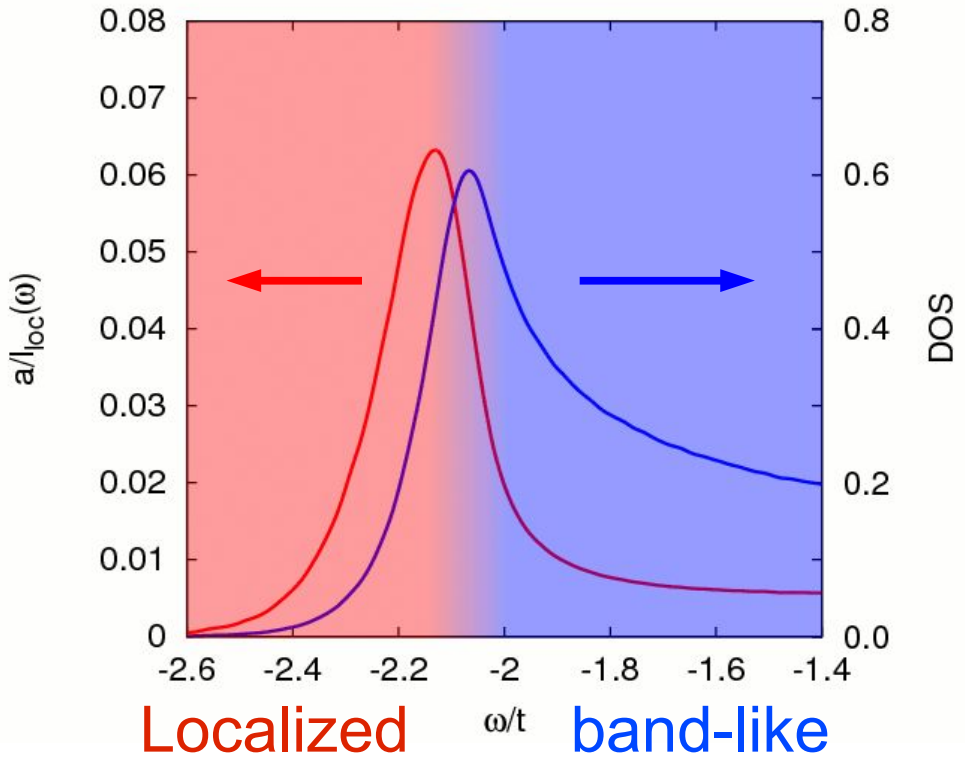
Band electrons (weakly renormalized)

Incoherent states (beyond band theory, no band dispersion)

A tail of localized states appears in the DOS well before the breakdown of the band description $l_{\mathrm{mfp}} < a \quad (s > t)$ (i.e. at all temperatures of interest)

→ dual nature of carriers

Localization length

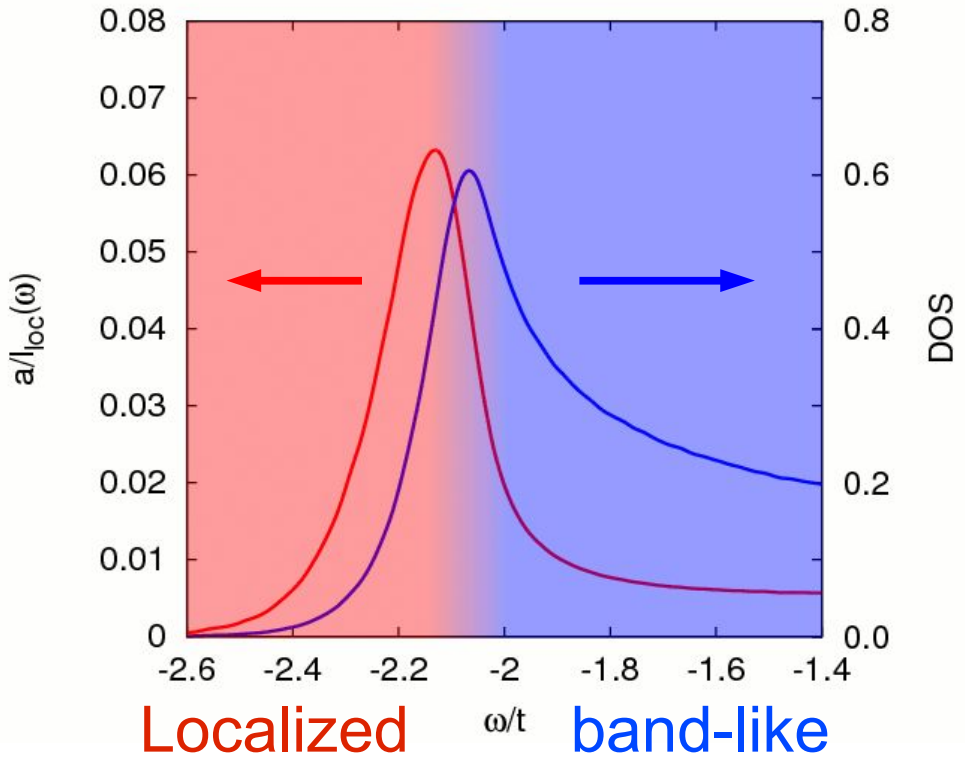


$$\rho(\omega) = \sum_k A(k,\omega)$$

$$\frac{1}{l_{loc}(\omega)} = \int d\omega' \rho(\omega)\rho(\omega') \log(|\omega - \omega'|/|\omega'|)$$

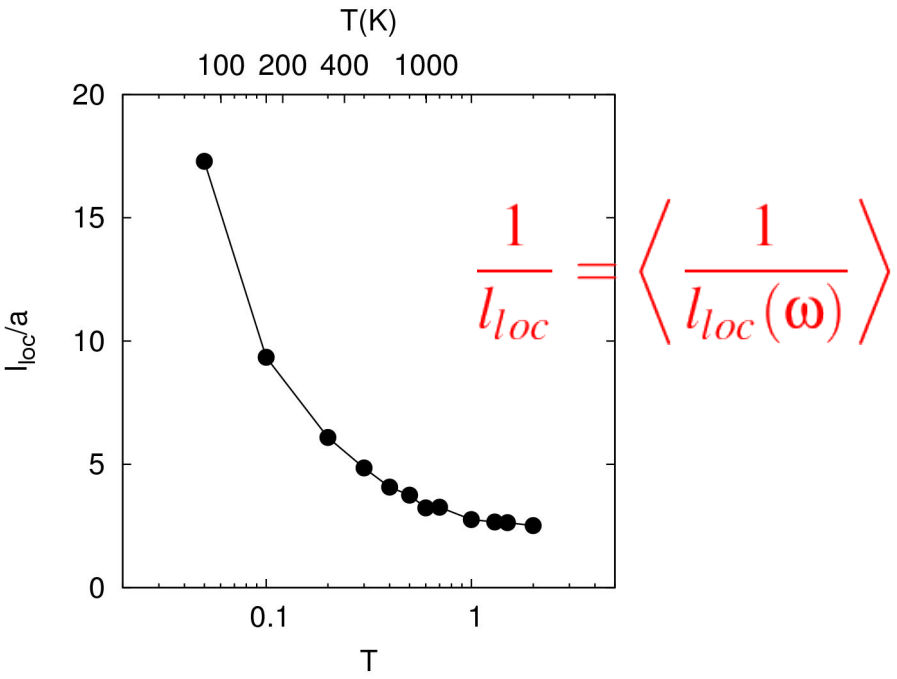
- Dual nature of the carriers shows up in (momentum/energy resolved) spectral properties (ARPES, DOS)

Localization length



$$\rho(\omega) = \sum_k A(k,\omega)$$

$$\frac{1}{l_{loc}(\omega)} = \int d\omega' \rho(\omega)\rho(\omega') \log(|\omega - \omega'|/|\omega'|)$$



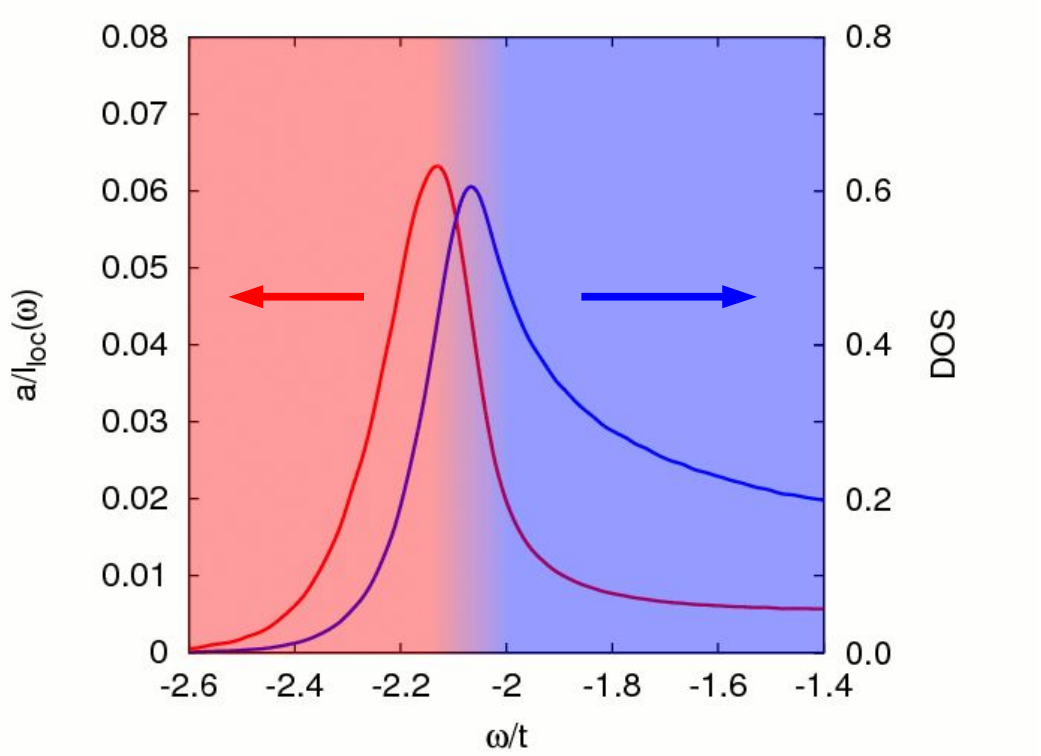
- Dual nature of the carriers shows up in (momentum/energy resolved) spectral properties (ARPES, DOS)

- Localized nature dominates (momentum/energy integrated) real-space probes

Mobility (Kubo)

$$\mu_{Kubo} \propto T^{-1} \int d\omega B(\omega) e^{-\omega/T}$$

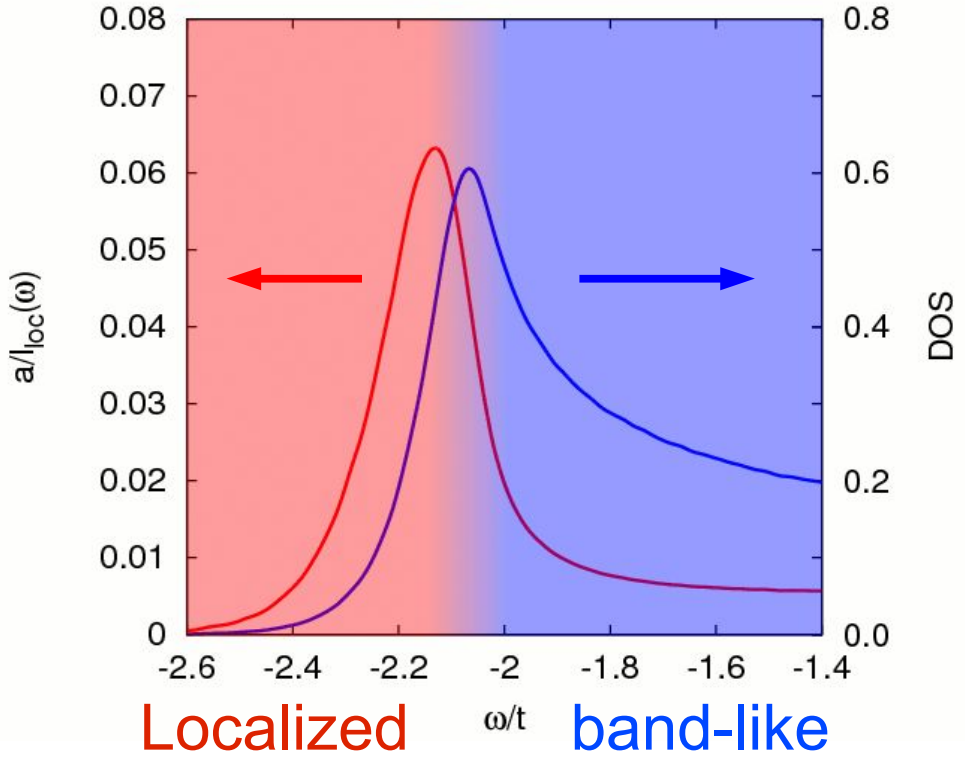
$B(\omega) = \langle JJ \rangle$ « energy resolved mobility »

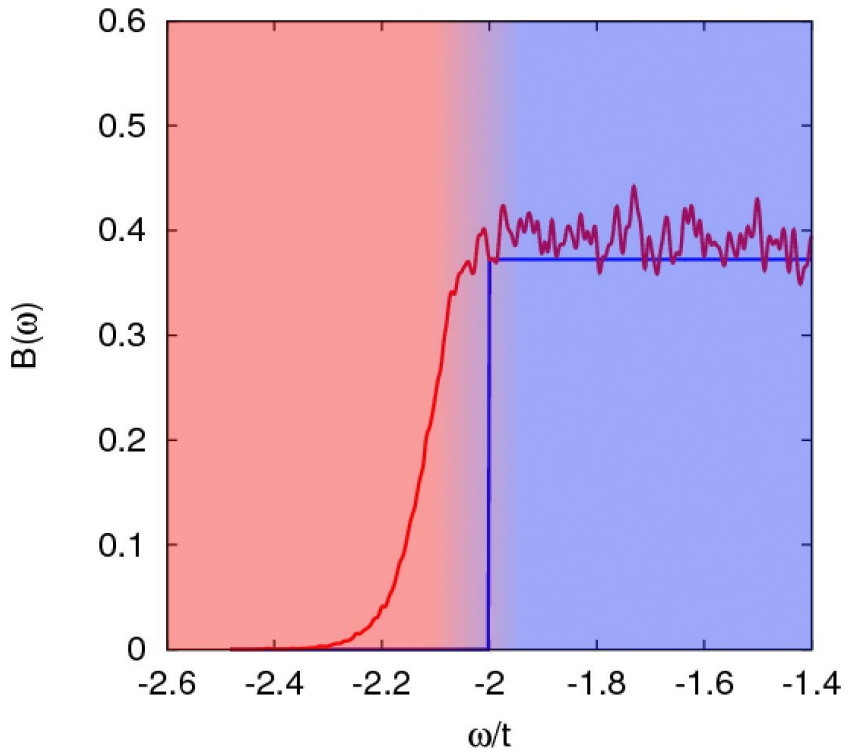


Mobility (Kubo)

$$\mu_{Kubo} \propto T^{-1} \int d\omega B(\omega) e^{-\omega/T}$$

$B(\omega) = \langle JJ \rangle$ « energy resolved mobility »





- The Kubo approach demonstrates that there are two separate contributions to the mobility: band electrons + incoherent tail states
- Relative importance tuned by temperature (statistical weight) $e^{-\omega/T}$

incoherent states → mobility saturation

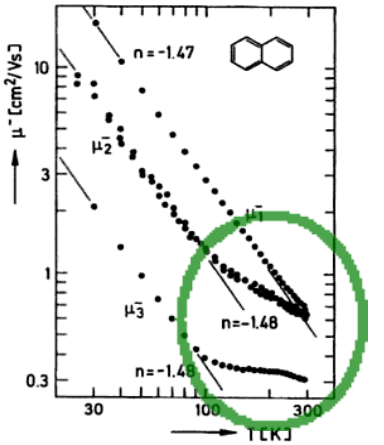
- All states become incoherent when $l_{\mathrm{mfp}} < a \quad (s > t)$
  - For incoherent states the scattering rate still increases with temperature but « saturates »

$\Gamma \propto \sqrt{\lambda \langle x^2 \rangle} \propto \sqrt{T}$ instead of $\Gamma \propto T$

[Millis PRL99]
[Gunnarsson Nature2000]

  - thermal fluctuations of crystal structure
    → additional phonon assisted hops $t^2 \sim T$

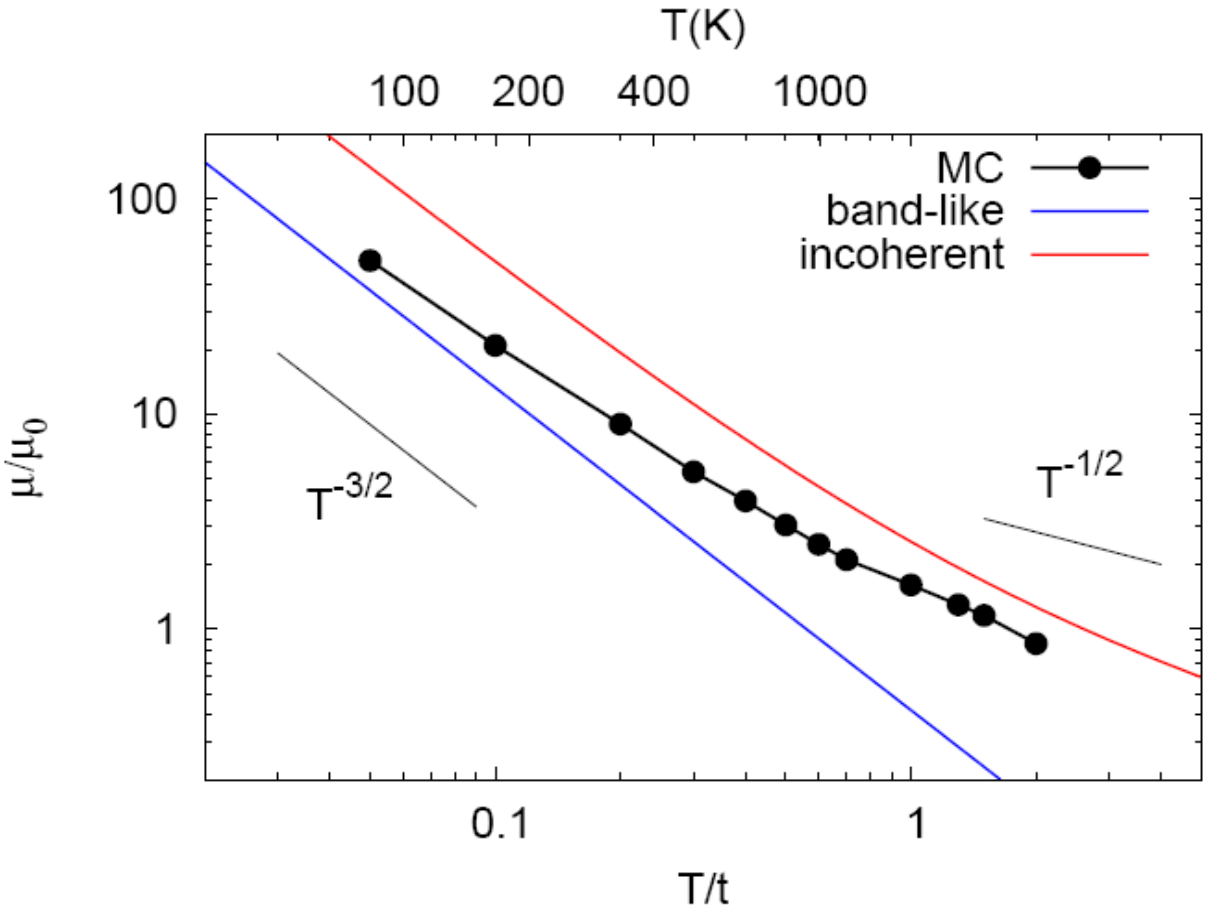
$$\mu \propto \frac{1}{T}\frac{t^2}{\Gamma} \sim \frac{T}{T\sqrt{T}} \sim T^{-1/2} \text{ instead of } T^{-2}$$



?

- breakdown of usual Boltzmann transport does not imply localization:
  weak e-ph coupling → no activated hopping
- gradual crossover between the two limits, intermediate behavior

Mobility (MC+Kubo)



- At temperatures of interest in OSC, transport occurs via both band conduction and incoherent conduction
- T dependence is intermediate (but no 1/T^2 behavior)

Conclusions

- The puzzle on the microscopic nature of carriers in crystalline organic semiconductors can be understood by observing that both band-like and localized excitations are simultaneously present in these systems due to the large thermal fluctuations of the lattice structure
- These two aspects show up differently according to the experimental probe (momentum space, real space)
- Transport mechanism: both band-like and localized states contribute. The mobility gradually crosses over with T from Boltzmann-like to a saturated behavior as $l_{\mathrm{mfp}} \sim a$ (but no localization).