Bandlike Motion and Mobility Saturation in Organic Molecular Semiconductors. Supplementary information.

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I. RECURSION FORMULAE FOR THE CALCULATION OF THE GREEN'S FUNCTION

The Green function of the problem is defined as

$$G_{i,j}(\omega, X) = \langle j| \frac{1}{\omega - H_{el}(X)} |i\rangle \tag{1}$$

where H_{el} is the first term appearing in Eq. (1) of the paper. In the site representation H_{el} is a tridiagonal matrix

$$\omega - H_{el}(X) = \begin{pmatrix} a_0 & b_0 & 0 & ... \\ b_0 & a_1 & b_1 & ... \\ ... & ... & ... & ... \\ ... & 0 & b_{N-1} & a_N \end{pmatrix} \tag{2}$$

where the diagonal and off-diagonal terms are respectively $a_i = \omega$ and $b_i = tf(X_i - X_{i+1})$. Diagonal elements can be easily obtained by calculating directly the inverse Eq. (1)[11]

$$G_{i,i} = \frac{1}{a_i - \Sigma_L^{(i)} - \Sigma_R^{(i)}} \tag{3}$$

where the *left* and *right* self-energies are respectively

$$\Sigma_L^{(i)} = \frac{b_{i-1}^2}{a_{i-1} - \Sigma_L^{(i-1)}} \tag{4}$$

and

$$\Sigma_R^{(i)} = \frac{b_i^2}{a_{i+1} - \Sigma_R^{(i+1)}}. \tag{5}$$

To control the finite size effects we choose to consider a chain which is attached to infinite *leads* both to the left and to the right. Each lead is a semi-infinite non-interacting chain. This results in the following boundary conditions

$$\Sigma_L^{(0)} = \Sigma_R^{(N-1)} = \frac{t^2}{2}(\omega - \sqrt{\omega^2 - 4t^2}), \tag{6}$$

Notice that the infinite continued fraction corresponding to each lead has been iterated analitically to give the square-root terms in Eqs. (6). The effect of this choice of boundary conditions is to regularize the DOS for a given realization of the thermal noise displacements $\{X_i\}$, especially at weak disorder strengths (i.e. weak λ and low temperature) as shown in 1.

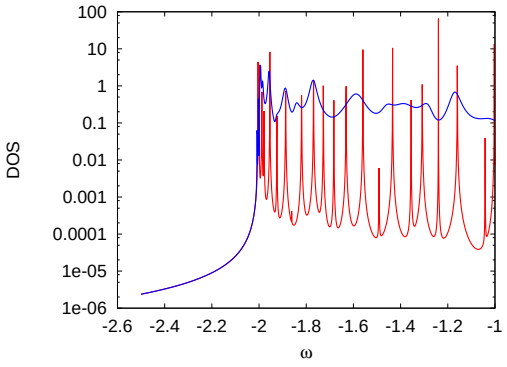

FIG. 1: DOS for a single realization of the displacements X_i at $\lambda = 0.01$ and $T = 0.2$ for a chain of $N = 64$ sites attached to two semi-infinite leads (blue) or with open boundary conditions. A finite broadening $\delta = 10^{-5}$ has been used to display the data.

Following Refs.[12,13] a symmetric tri-diagonal matrix $\omega - H_{el}$ can be analitically inverted to obtain all the off-diagonal terms through recursion formulas expressed in terms of ratios of polynomials in ω. However these formulas are not numerically stable at large frequencies. We derive instead the following recursion formulas

$$G_{i-1,j} = \left(-\frac{\Sigma_L^{(i)}}{b_{i-1}}\right) G_{i,j} \qquad i \le j \tag{7}$$

$$G_{i+1,j} = \left(-\frac{\Sigma_R^{(i)}}{b_i}\right) G_{i,j} \qquad i \ge j \tag{8}$$

by which the off-diagonal elements are readily obtained once the diagonal part of the Green's function is known through Eq. (3).

II. SPREAD OF THE ELECTRONIC WAVE-FUNCTION

The localization length of the electronic wave-function in a disordered system can be defined as the rate of decay

of a given eigenvector $\psi_\gamma(i)$ as a function of the distance $i = 0, N-1$ on the lattice:

$$\frac{1}{l_\gamma} = -\lim_{N\to\infty} \frac{1}{N-1} \log|\psi_\gamma(0)\psi^*_\gamma(N-1)|. \quad (9)$$

In our case the $\psi_\gamma(i)$ are solutions of the Schrödinger equation for the carrier

$$-t\sum_j^{(i)} [1 - g(X_i - X_j)]\,\psi_\gamma(j) = E_\gamma \psi_\gamma(i) \quad (10)$$

for a *given* set of displacements X_i. The parameters in Eq. (10) are defined in the text and $\sum_j^{(i)}$ means the sum over the neighbors of the site i. Following Ref.[8] together with the sum rule demonstrated in Ref.[9] and the spectral representation $\rho(\omega) = -Im\sum_{i=0}^{N-1} G_{i,i}(\omega)/\pi$ in terms of the local Green's function we get[9],

$$\frac{1}{l_\gamma} = \int d\omega' \rho(\omega') \log(|E_\gamma - \omega'|/|\omega'|). \quad (11)$$

It can be noted that while $\rho(\omega)$ in Eq. (11) is a self-averaging property, since it can be expressed as an average over the sets of static displacements X_i, the quantity l_γ still depends on random energies E_γ [see Eq. (10)].

The concept of localization length of a particular state studied in Refs.[8][9] can be generalized to that of a density of states around a given energy ω

$$\frac{1}{l_{loc}(\omega)} = \sum_\gamma \frac{1}{l_\gamma}\delta(\omega - E_\gamma), \quad (12)$$

which can be expressed via the spectral function as

$$\frac{1}{l_{loc}(\omega)} = \int d\omega' \rho(\omega)\rho(\omega') \log(|\omega - \omega'|/|\omega'|) \quad (13)$$

Notice that contrary to l_γ, $l_{loc}(\omega)$ is a self-averaging property.

We are considering a system in which the lattice vibrations behave as classical variables owing to the low phonon frequencies involved. Still, the lattice displacements are able to move on the timescales of observation due to their intrinsically dynamical nature. This corresponds to the case of an "annelaed" disorder, which is able to relax (thermalize) towards an equilibrium thermal distribution: localized states appear for each given realization of the disorder (i.e. at each given time of the thermal lattice evolution), but true localization is prevented *on the long time* as the localization center randomly diffuses following the thermal fluctuations of the lattice.

It is known that in such adiabatic regime a good approximation for the ground-state can be obtained based on the static phonon limit, by periodizing appropriately the localized wave-function in order to restore the translational invariance[10]. In that case the localization length obtained from the static phonon treatment correctly gives the extension of the carrier wave-function around a given displaced set of oscillators. Following this argument we evaluate the typical extension of the wave-function of the diffusing carrier by performing the following thermal average of the localization length Eq. (13):

$$\frac{1}{l_{loc}} = \frac{1}{Z}\int d\omega d\omega' e^{-\beta\omega}\rho(\omega)\rho(\omega')\log(|\omega - \omega'|/|\omega'|) \quad (14)$$

with Z the partition function of the carrier

$$Z = \int d\omega \rho(\omega) e^{-\beta\omega}. \quad (15)$$

The quantity $1/l_{loc}$ is illustrated in Fig. 1c of the main text.

III. CALCULATION OF THE MOBILITY VIA THE KUBO FORMULA

We calculate the carrier mobility using the Kubo formula expressed in terms of the exact electron propagators, neglecting vertex corrections. In the case of the model Eq. (1) this amounts to replacing the function $B(\omega)$ appearing in Eq. (2) of the main text by the factorized "bubble"

$$B(\omega) = \sum \langle\rho_{i,j}(\omega)\rangle\langle\rho_{k,l}(\omega)\rangle\langle J_{j,k}J_{l,i}\rangle. \quad (16)$$

The sum in Eq.(16) extends to all site indices, $J_{k,l} = \langle k|J|l\rangle$ is the matrix element of the current operator $J = \sum_i c_i^\dagger c_{i-1} - c_i^\dagger c_{i+1}$ between single-particle states $|l\rangle = c_l^\dagger|0\rangle$, ρ is the imaginary part of the Green's function $\rho_{i,j}(\omega) = -ImG(i,j,\omega)/\pi$ and $\langle\ldots\rangle$ has the meaning of an average over the static phonon variables X_i. Due to the Gaussian nature of the displacements this average can be performed analitically in the last term of Eq. (16) so that $B(\omega)$ and μ can be calculated via the knowledge of the averaged Green's function $\langle\rho_{i,j}(\omega)\rangle$ alone.

The neglect of vertex corrections as carried out here has been shown to provide essentially exact results in the case of momentum-independent electron-lattice interactions in three dimensions[5]. In the present case this approximation is justified once we consider the dynamic nature of the disorder induced by the thermal lattice motion. Indeed, the genuine localization characteristic of disordered one-dimensional systems is lost at length-scales larger than ℓ ($\ell/a = \sqrt{2\pi\mu k_B T/\mu_0\hbar\omega_0} \simeq 20$ in our case), which is the distance traveled by the electron before the disordered landscape is modified by the lattice dynamics. Beyond such distances localization corrections become unimportant, justifying a "bubble" calculation of the mobility similar to that of Refs.[6,7]. As we show below, the neglect of vertex corrections in that case is equivalent to setting the transport scattering time equal to the quasiparticle lifetime and leads to an overestimate of the

mobility by at most a factor of 2 in the low temperature band limit, while such corrections become ininfluent in the high temperature saturated regime. Apart from numerical factors, the present approximation therefore captures the essential aspects of the transport mechanism (especially regarding its temperature dependence), which stem directly from the dual nature of the *single-particle* electron states.

IV. LIMITING BEHAVIORS OF THE CARRIER MOBILITY

A. Band-like transport

In the Boltzmann description of electronic transport in nondegenerate semiconductors, the mobility is expressed as

$$\mu(T) = \frac{e}{nk_BT}\sum_k v_k^2 \tau_k^{tr} e^{-(\epsilon_k-\mu)/k_BT} \tag{17}$$

where τ_k^{tr} and v_k are respectively the transport scattering time and the band velocity for electrons of momentum k, μ is the chemical potential and $n = \sum_k e^{-(\epsilon_k-\mu)/T}$ the thermally activated carrier density. In the quasi-elastic limit where the phonon frequency sets the smallest energy scale in the problem, $\hbar\omega_0 \ll T, t$ the scattering time is defined as

$$1/\tau_k^{tr} = \frac{2k_BT}{\hbar\omega_0}\int dq\; g_{k,k+q}^2(1-\cos\theta_{k,k+q})\;\delta(\epsilon_k-\epsilon_{k+q}) \tag{18}$$

with $g_{k,k+q} = 2ig[\sin(k+q)-\sin(k)]$ the Fourier transform of the off-diagonal electron-lattice coupling and $\theta_{k,k+q}$ the angle between the incoming and outcoming momentum states. Dropping this angular factor corresponds to the neglect of ladder-type vertex corrections in the Kubo formulation, which amounts to replace the transport scattering rate by the quasiparticle scattering rate $1/\tau_k$. The resulting mobility is therefore overestimated by a factor of 2, as it can be easily shown that $\tau_k^{tr} = \tau_k/2$ in the present model.

The integral in Eq. (18) can be carried out analytically, yielding

$$\mu = \frac{\mu_0}{16\pi\lambda}\frac{t}{T}\frac{\sinh(2t/T)}{I_0(2t/T)}, \tag{19}$$

with $\mu_0 = ea^2/\hbar$ and I_0 the modified Bessel function. It is worth noting that the present result can be straightforwardly generalized to the case of a finite phonon frequency $\omega_0 \neq 0$, and Eq. (19) is correctly recovered in the limit $\omega_0/T \ll 1$, independently of the value of t. In the limiting cases of temperatures much lower or much higher than the bandwidth, the above expression reduces to the following power laws[1,2]:

$$\mu = \frac{\mu_0}{8\sqrt{\pi}\lambda}\left(\frac{t}{k_BT}\right)^{3/2} \qquad k_BT \ll 2t \tag{20}$$

$$\mu = \frac{\mu_0}{4\pi\lambda}\left(\frac{t}{k_BT}\right)^{2} \qquad k_BT \gg 2t \tag{21}$$

For comparison with the numerical data presented in Fig.2 of the manuscript, the blue line is the mobility evaluated from Boltzmann theory without the angular factor $1-\cos\theta_{k,k+q}$, with the carrier density $n = \sum_k e^{-(\tilde{\epsilon}_k-\mu)/T}$ evaluated in terms of the renormalized band dispersion $\tilde{\epsilon}_k = \epsilon_k/(1-2\lambda k_BT/t)$ as obtained from second order perturbation theory (such band renormalization is visible in Fig. 1a of the main text[16]), which yields a constant correction factor to the mobility $\mu \to \mu e^{4\lambda}$.

B. Incoherent transport

In the large scattering limit, the theory of band conduction presented above breaks down due to the complete loss of momentum conservation. This happens when the apparent mean-free-path for band electrons reduces to values below the inter-molecular spacing (this essentially coincides with the conditions that the one-electron lifetime $\tau < t^{-1}$, or equivalently that the average thermal fluctuations of the transfer integrals, $s = \sqrt{8\lambda tT}$, exceed the mean value t, as obtained respectively in the limits of weak and strong disorder). In this case a different mechanism of charge transport sets in where Bloch waves are replaced by fully incoherent states diffusing from site to site as in a classical random walk. The corresponding mobility can be evaluated via the Kubo formula, observing that the spectral function $A(k,\omega)$ becomes k-independent (any information on the dispersion of momentum states is lost) and tends to a gaussian[3,4,7]

$$\rho(\omega) = \frac{1}{\sqrt{2\pi s^2}}e^{-\omega^2/2s^2} \tag{22}$$

whose variance $s = \sqrt{8\lambda tT}$ is determined by the average thermal fluctuations of the transfer integral (this result can be generalized to include quantum fluctuations in the case of a finite phonon frequency ω_0, in which case $s = \sqrt{4\lambda t\coth(\omega_0/2T)}$, see Refs.[14,15]). This can be inserted into the Kubo formula for the mobility

$$\mu = \mu_0\frac{\pi\xi(T)}{nT}\int d\omega\rho(\omega)^2 e^{-(\omega-\mu)/k_BT} \tag{23}$$

with $n = \int d\omega\rho(\omega)e^{-(\omega-\mu)/k_BT}$ and $\xi(T) = 1+4\lambda k_BT/t$ a prefactor that accounts for the temperature dependence of the current operator, i. e. the thermally assisted tunneling caused by the thermal fluctuations of the transfer integrals. Performing the integral in the limit $\omega_0 \ll T$ we obtain

$$\mu_{\rm incoh} = \frac{\sqrt{\pi/8}}{\sqrt{\lambda}}\left(\frac{t}{T}\right)^{3/2}\left(1+4\lambda\frac{k_BT}{t}\right) \tag{24}$$

which is displayed in Fig.2 of the manuscript, and recovers the high temperature behavior of the numerical data.

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[16] Note that contrary to common claims of bandwidth narrowing in these systems, an adiabatic treatment of the electron-lattice interactions as appropriate in the presence of slow lattice fluctuations shows that the electronic bands actually get broader in the presence of interactions.