Supplemental Material for
Charge transport limited by nonlocal electron–phonon interaction. I. Hierarchical equations of motion approach

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SI. INFERRING THE GENERALIZED WICK'S THEOREM FROM THE DYNAMICAL EQUATIONS OF THE HEOM METHOD

Taking the time derivative of

$$\rho_{\mathbf{n}}^{(n)}(t) = \mathrm{Tr}_{\mathrm{ph}}\left\{F_{\mathbf{n}}^{(n)}\rho_{\mathrm{tot}}(t)\right\}, \tag{S1}$$

and using the Liouville equation $\partial_t\rho_{\mathrm{tot}}(t) = -i[H_{\mathrm{tot}},\rho_{\mathrm{tot}}(t)]$ for the density operator of the interacting carrier–phonon system, one obtains

$$\begin{aligned}\partial_t\rho_{\mathbf{n}}^{(n)}(t) =& -i[H_{\mathrm{e}},\rho_{\mathbf{n}}^{(n)}(t)]\\ &- i\mathrm{Tr}_{\mathrm{ph}}\left\{[F_{\mathbf{n}}^{(n)},H_{\mathrm{ph}}]\rho_{\mathrm{tot}}(t)\right\}\\ &- i\mathrm{Tr}_{\mathrm{ph}}\left\{F_{\mathbf{n}}^{(n)}[H_{\mathrm{e-ph}},\rho_{\mathrm{tot}}(t)]\right\}.\end{aligned} \tag{S2}$$

In the second term on the RHS of Eq. (S2), we performed a cyclic permutation of phonon operators under the partial trace over phonons. Inserting $H_{\mathrm{e-ph}} = \sum_{qm} V_q f_{qm}$ into the third term on the RHS of Eq. (S2), and performing appropriate cyclic permutations of phonon operators, we transform Eq. (S2) into

$$\begin{aligned}\partial_t\rho_{\mathbf{n}}^{(n)}(t) =& -i[H_{\mathrm{e}},\rho_{\mathbf{n}}^{(n)}(t)]\\ &- i\mathrm{Tr}_{\mathrm{ph}}\left\{[F_{\mathbf{n}}^{(n)},H_{\mathrm{ph}}]\rho_{\mathrm{tot}}(t)\right\}\\ &- i\sum_{qm} V_q\mathrm{Tr}_{\mathrm{ph}}\left\{F_{\mathbf{n}}^{(n)}f_{qm}\rho_{\mathrm{tot}}(t)\right\}\\ &+ i\sum_{qm}\mathrm{Tr}_{\mathrm{ph}}\left\{f_{qm}F_{\mathbf{n}}^{(n)}\rho_{\mathrm{tot}}(t)\right\}V_q.\end{aligned} \tag{S3}$$

On the other hand, using $\langle f_{q_2m_2}f_{q_1m_1}\rangle_{\mathrm{ph}} = \delta_{m_1\overline{m_2}}\eta_{q_2q_1m_2}$ and $\langle f_{q_1m_1}f_{q_2m_2}\rangle_{\mathrm{ph}} = \delta_{m_1\overline{m_2}}\eta^*_{\overline{q_2}\,\overline{q_1}\,\overline{m_2}}$, we transform the HEOM in Eq. (5) of the main text into

$$\begin{aligned}\partial_t\rho_{\mathbf{n}}^{(n)}(t) =& -i[H_{\mathrm{e}},\rho_{\mathbf{n}}^{(n)}(t)] - \mu_{\mathbf{n}}\rho_{\mathbf{n}}^{(n)}(t)\\ &- i\sum_{qm}V_q\left[\rho_{\mathbf{n}_{qm}^+}^{(n+1)}(t) + \sum_{q'm'}n_{q'm'}\langle f_{q'm'}f_{qm}\rangle_{\mathrm{ph}}\rho_{\mathbf{n}_{q'm'}^-}^{(n-1)}(t)\right]\\ &+ i\sum_{qm}\left[\rho_{\mathbf{n}_{qm}^+}^{(n+1)}(t) + \sum_{q'm'}n_{q'm'}\langle f_{qm}f_{q'm'}\rangle_{\mathrm{ph}}\rho_{\mathbf{n}_{q'm'}^-}^{(n-1)}(t)\right]V_q.\end{aligned} \tag{S4}$$

The first terms on the RHSs of Eqs. (S3) and (S4) are identical. The commutator $[F_{\mathbf{n}}^{(n)},H_{\mathrm{ph}}]$ is a purely phononic operator that describes an n-phonon-assisted process (H_{ph} conserves the number of phonons). Irrespective of the particular form of $F_{\mathbf{n}}^{(n)}$, it is clear that the commutator $[F_{\mathbf{n}}^{(n)},H_{\mathrm{ph}}]$ is proportional to $F_{\mathbf{n}}^{(n)}$ itself, thus the second

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terms of the RHSs of Eqs. (S3) and (S4) have to be identical. The simplest possibility that the sum of the third and the fourth terms of Eq. (S3) is identical to the sum of the third and the fourth terms of Eq. (S4) is that

$$\mathrm{Tr}_{\mathrm{ph}}\left\{F_{\mathbf{n}}^{(n)} f_{qm}\rho_{\mathrm{tot}}(t)\right\} = \rho_{\mathbf{n}_{qm}^{+}}^{(n+1)}(t) + \sum_{q'm'} n_{q'm'}\langle f_{q'm'} f_{qm}\rangle_{\mathrm{ph}}\rho_{\mathbf{n}_{q'm'}^{-}}^{(n-1)}(t), \tag{S5}$$

$$\mathrm{Tr}_{\mathrm{ph}}\left\{f_{qm} F_{\mathbf{n}}^{(n)} \rho_{\mathrm{tot}}(t)\right\} = \rho_{\mathbf{n}_{qm}^{+}}^{(n+1)}(t) + \sum_{q'm'} n_{q'm'}\langle f_{qm} f_{q'm'}\rangle_{\mathrm{ph}}\rho_{\mathbf{n}_{q'm'}^{-}}^{(n-1)}(t). \tag{S6}$$

The generalized Wick's theorem embodied in Eqs. (14) and (15) of the main text then follows by making use of Eq. (S1) on the right-hand sides of Eqs. (S5) and (S6), respectively.

SII. IMPLICATIONS OF THE TIME-REVERSAL SYMMETRY FOR THE CROSS CONTRIBUTION TO THE CURRENT–CURRENT CORRELATION FUNCTION

The proof that $\langle j_\mathrm{e}(t) j_\mathrm{e-ph}(0)\rangle = \langle j_\mathrm{e-ph}(t) j_\mathrm{e}(0)\rangle$ relies on general properties of equilibrium correlation functions and the time-reversal operator.

The equilibrium correlation function of hermitean operators A_2 and A_1 satisfies

$$\langle A_2(t)A_1(0)\rangle = \langle A_1(-t)A_2(0)\rangle^*. \tag{S7}$$

The time-reversal operator $\mathcal{I}_t$ is an antiunitary (antilinear and unitary, $\mathcal{I}_t^{-1} = \mathcal{I}_t^\dagger$), involutive ($\mathcal{I}_t^2 = 1$), and thus hermitean ($\mathcal{I}_t^\dagger = \mathcal{I}_t$) operator that acts on the free-electron states $|k\rangle$ as $\mathcal{I}_t|k\rangle = |\overline{k}\rangle$, while its action on phonon creation and annihilation operators is $\mathcal{I}_t b_q^{(\dagger)} \mathcal{I}_t = b_{\overline{q}}^{(\dagger)}$. The Hamiltonian H_tot [Eqs. (1)–(3) of the main text] is invariant under time reversal, i.e., $\mathcal{I}_t H_\mathrm{tot} \mathcal{I}_t = H_\mathrm{tot}$. Using the definition of current operators j_e [Eq. (20) of the main text] and $j_\mathrm{e-ph}$ [Eqs. (21)–(23) of the main text], one obtains that

$$\mathcal{I}_t j_\mathrm{e/e-ph} \mathcal{I}_t = -j_\mathrm{e/e-ph}. \tag{S8}$$

Using the decomposition $\mathcal{I}_t = UK$, where K denotes complex conjugation, while U is a unitary operator, one proves that

$$\mathrm{Tr}\left\{\mathcal{I}_t A \mathcal{I}_t\right\} = \mathrm{Tr}\left\{A\right\}^*. \tag{S9}$$

We perform the following transformations

$$\langle j_\mathrm{e}(t) j_\mathrm{e-ph}(0)\rangle = \langle j_\mathrm{e-ph}(-t) j_\mathrm{e}(0)\rangle^* = \langle \mathcal{I}_t j_\mathrm{e-ph}(-t) \mathcal{I}_t \mathcal{I}_t j_\mathrm{e} \mathcal{I}_t\rangle = (-1)^2 \langle j_\mathrm{e-ph}(t) j_\mathrm{e}(0)\rangle. \tag{S10}$$

The first equality follows from Eq. (S7). To establish the second equality, we combine Eq. (S9) and the invariance of H_tot under time reversal. The third equality makes use of the antilinearity of $\mathcal{I}_t$ and Eq. (S8).

SIII. DETAILS OF HEOM COMPUTATIONS

In this section, N denotes the chain length, D is the maximum hierarchy depth, t_{max} is the maximum (real) time up to which HEOM are propagated, while δ_{OSR} [Eq. (51) of the main text] is the relative accuracy with which the optical sum rule is satisfied. Our HEOM data are openly available in Ref. 1.

ω_0/J	λ	T/J	N	D	t_{max}	δ_{OSR}
1	0.05	1	160	1	500	9.3×10^{-4}
1	0.05	2	160	2	300	1.15×10^{-3}
1	0.05	5	71	3	150	4×10^{-6}
1	0.05	10	45	4	100	8×10^{-5}
1	0.25	1	45	4	200	10^{-3}
1	0.25	2	45	4	70	4.5×10^{-4}
1	0.25	5	10	7/8	100	6.6×10^{-5}
1	0.25	$10^{0.8}$	10	7/8	100	7.1×10^{-5}
1	0.25	$10^{0.9}$	10	7/8	100	7.5×10^{-5}
1	0.25	10	7	7/8	100	8×10^{-5}
1	0.5	1	21	6	70	6×10^{-4}
1	0.5	2	15	6	100	1.9×10^{-4}
1	0.5	5	10	7/8	50	1.2×10^{-4}
1	0.5	$10^{0.8}$	10	7/8	50	1.3×10^{-4}
1	0.5	$10^{0.9}$	8	8/9	50	1.4×10^{-4}
1	0.5	10	7	8/9	50	1.6×10^{-4}
1	1	1	13	8	12	1.9×10^{-3}
1	1	2	13	8	15	2.1×10^{-5}
1	1	5	9	9/10	15	3.5×10^{-4}
1	1	$10^{0.8}$	8	10/11	15	3.9×10^{-4}
1	1	$10^{0.9}$	7	11/12	15	4.7×10^{-4}
1	1	10	7	11/12	10	7.0×10^{-4}

TABLE S1. Details of the HEOM computations performed for $\omega_0/J = 1$.

ω_0/J	λ	T/J	N	D	t_{max}	δ_{OSR}
3	0.05	2	161	2	1000	2.3×10^{-4}
3	0.05	5	121	2	400	1.0×10^{-4}
3	0.05	10	91	2	100	2.2×10^{-4}
3	0.25	2	31	3	1000	3.6×10^{-4}
3	0.25	5	21	5	30	2.1×10^{-4}
3	0.25	$10^{0.8}$	19	5	30	2.2×10^{-4}
3	0.25	$10^{0.9}$	17	5	30	2.4×10^{-4}
3	0.25	10	15	5	30	2.5×10^{-4}
3	0.5	2	21	5	500	1.4×10^{-4}
3	0.5	5	15	6	25	2.4×10^{-4}
3	0.5	$10^{0.8}$	13	6/7	25	2.6×10^{-4}
3	0.5	$10^{0.9}$	10	7/8	25	2.8×10^{-4}
3	0.5	10	10	7/8	20	3.6×10^{-4}
3	1	2	13	5	500	2.9×10^{-3}
3	1	5	13	6/7	110	1.2×10^{-4}
3	1	$10^{0.8}$	13	6/7	110	1.2×10^{-4}
3	1	$10^{0.9}$	10	8/9	30	2.4×10^{-4}
3	1	10	10	8/9	20	3.7×10^{-4}

TABLE S2. Details of the HEOM computations performed for $\omega_0/J = 3$.

SIV. POWER-LAW FITS OF THE TEMPERATURE-DEPENDENT MOBILITY IN THE REGIME OF PHONON-ASSISTED TRANSPORT

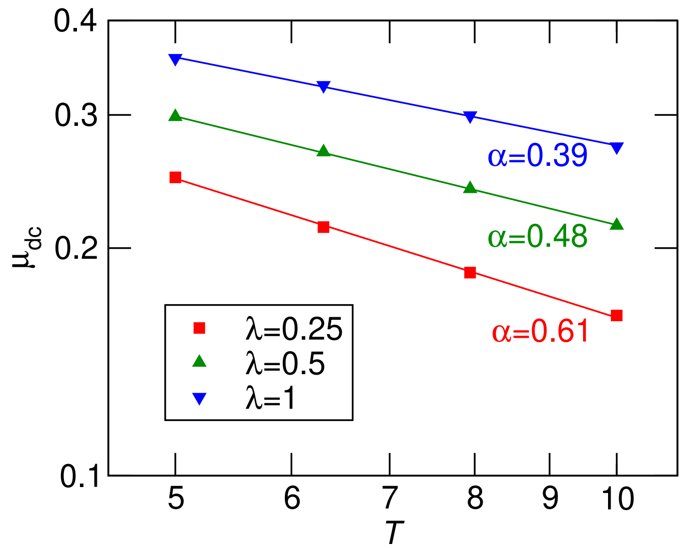

FIG. S1. HEOM results for $\mu_{\rm dc}(T)$ (symbols) and their best fits to the power-law function $\mu_{\rm dc}(T) = A/T^{\alpha}$ with two parameters, the amplitude A and the power-law exponent α. The fits are performed for $\omega_0 = J = 1$, in parameter regimes in which the phonon-assisted share of the HEOM mobility is $\gtrsim 50\%$ and the magnitude of the cross share is $\lesssim 10\%$, see Figs. 4 (b) and 4 (c) of the main text. The values of α are cited next to each dataset. Note the logarithmic scale on both axes.

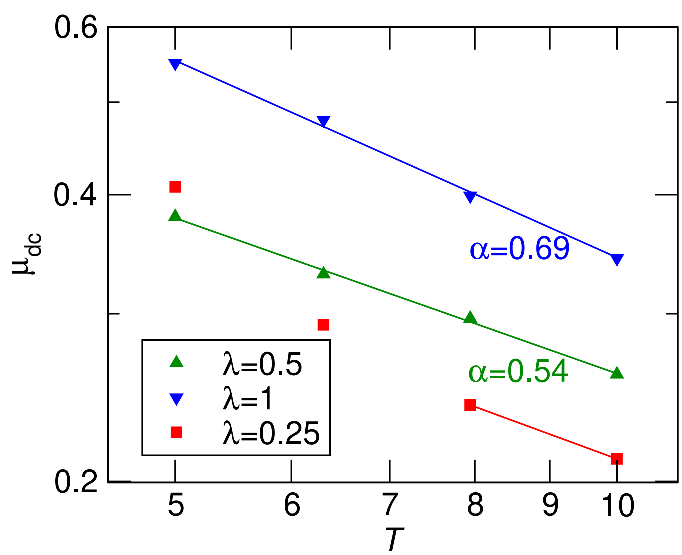

FIG. S2. HEOM results for $\mu_{\rm dc}(T)$ (symbols) and their best fits to the power-law function $\mu_{\rm dc}(T) = A/T^{\alpha}$ with two parameters, the amplitude A and the power-law exponent α. The fits are performed for $\omega_0 = 3$ and $J = 1$, in parameter regimes in which the phonon-assisted share of the HEOM mobility is $\gtrsim 50\%$ and the magnitude of the cross share is $\lesssim 10\%$, see Figs. 6 (b) and 6 (c) of the main text. The values of α are cited next to each dataset. For completeness, we also show HEOM data for $\lambda = 0.25$. These can be fitted to the power-law function only when the magnitude of the cross contribution falls below $\sim 10\%$, which happens at sufficiently high temperatures, see the red line connecting the last two squares and Fig. 6 (c) of the main text. Note the logarithmic scale on both axes.

SV. EVALUATING THE BOLTZMANN-EQUATION COLLISION INTEGRAL USING THE HEOM FORMALISM

Here, we obtain the collision integral $\left(\frac{\partial p_k}{\partial t}\right)_{\mathrm{e-ph}}$ for the carrier–phonon scattering in the Boltzmann approach starting from the HEOM. Taking the matrix element $\langle k|\ldots|k\rangle$ of Eq. (5) of the main text for $\mathbf{n}=0$ and $n=0$, we obtain that the change in the population $p_k(t)=\langle k|\rho(t)|k\rangle$ of the free-carrier state $|k\rangle$ due to the carrier–phonon interaction is

$$\left(\frac{\partial p_k}{\partial t}\right)_{\mathrm{e-ph}} = -2\sum_{qm}\mathrm{Im}\,\left\{M(k,q)p^{(1)}_{k,qm}(t)\right\}, \tag{S11}$$

where we define

$$p^{(1)}_{k,qm}(t)=\langle k|\rho^{(1)}_{\mathbf{0}^+_{qm}}(t)|k+q\rangle. \tag{S12}$$

To arrive at Eq. (S11), we use $\rho^{(1)}_{\mathbf{0}^+_{\overline{qm}}}(t)=\rho^{(1)}_{\mathbf{0}^+_{qm}}(t)^\dagger$. Taking the matrix element $\langle k|\ldots|k+q\rangle$ of Eq. (5) of the main text for $\mathbf{n}=\mathbf{0}^+_{qm}$ and $n=1$, and neglecting the coupling to HEOM auxiliaries at depth 2, we obtain the following equation for $p^{(1)}_{k,qm}(t)$:

$$\partial_t p^{(1)}_{k,qm}(t) = -i\left(\varepsilon_k-\varepsilon_{k+q}-i\mu_m\right)p^{(1)}_{k,qm}(t) - iM(k,q)^*\left[c_m p_{k+q}(t)-c^*_{\overline{m}}p_k(t)\right]. \tag{S13}$$

Integrating Eq. (S13) in the Markov approximation $p_k(t-s)\approx p_k(t)$ yields

$$p^{(1)}_{k,qm}(t) = -iM(k,q)^*\left[c_m p_{k+q}(t)-c^*_{\overline{m}}p_k(t)\right]\int_0^t ds\, e^{-i(\varepsilon_k-\varepsilon_{k+q}-i\mu_m)s}. \tag{S14}$$

In the adiabatic approximation, one solves the integral in Eq. (S14) by letting $t\to+\infty$ to finally obtain ($\eta\to+0$)

$$p^{(1)}_{k,qm}(t) = M(k,q)^*\frac{c_m p_{k+q}(t)-c^*_{\overline{m}}p_k(t)}{\varepsilon_k-\varepsilon_{k+q}-i\mu_m-i\eta}. \tag{S15}$$

Inserting Eq. (S15) into Eq. (S11) and using $c^*_{\overline{m}}=c_{\overline{m}}$ and $\mathrm{Im}\,\frac{1}{\varepsilon_k-\varepsilon_{k+q}-i\mu_m-i\eta}=\pi\delta(\varepsilon_k-\varepsilon_{k+q}-i\mu_m)$ yields the following equation for $p_k(t)$:

$$\left(\frac{\partial p_k}{\partial t}\right)_{\mathrm{e-ph}} = -\sum_q w_{k+q,k}p_k(t)+\sum_q w_{k,k+q}p_{k+q}(t), \tag{S16}$$

where the transition rate from state $|k\rangle$ to state $|k+q\rangle$ is given in Eq. (E3) of the main text.

[1] V. Janković, Numerical investigation of transport properties of the one-dimensional Peierls model based on the hierarchical equations of motion, 10.5281/zenodo.14637019 (2025).