Detecting superconductivity out-of-equilibrium

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Recent pump-probe experiments on underdoped cuprates and similar systems suggest the existence of a transient superconducting state above $T_c$. This poses the question how to reliably identify the emergence of long-range order, in particular superconductivity, out-of-equilibrium. We investigate this point by studying a quantum quench in an extended Hubbard model and by computing various observables, which are used to identify (quasi-)long-range order in equilibrium. Our findings imply that, in contrast to current experimental studies, it does not suffice to study the time evolution of the optical conductivity to identify superconductivity. In turn, we suggest to utilize time-resolved ARPES experiments to probe for the formation of a condensate in the two-particle channel.

Introduction  Superconductivity (SC) is one of the hallmarks of condensed-matter systems and has inspired researchers since its discovery in 1911, and later by the advent of high-temperature SC in cuprate materials [1–4]. While, in particular for the latter class of materials, many questions are subject of ongoing research, the basic characteristics of the SC phase are by now well established as long as the system is in equilibrium. However, recent experiments (e.g., [5–9] on copper oxides, or on K3C60) report the observation of possible photo-induced transient SC phases, which can exist at elevated temperatures, even above the equilibrium-critical temperature $T_c$ [10–12]. In these investigations, ultrashort THz pulses excite single phonon modes, which decay very slowly compared to the typical time scale of the electron dynamics and thereby offer the possibility to control the interaction parameters of the electronic system [13]. Subsequently, the $\omega$-dependent optical conductivity is determined as a function of time via reflectivity measurements using a probe pulse, and SC correlations are identified by the emergence or enhancement of a signal at $\omega \to 0$. This is by now a standard experimental procedure, which, however, leaves many questions open, in particular concerning the characterization of the state induced by the pump excitation (see, e.g., Refs. 14–17). Recently, non-equilibrium Higgs oscillations have been suggested as a probe for the existence of a SC condensate [18].

In this Letter, we address this issue regarding further experimental measures to probe SC in such non-equilibrium setups. For the sake of simplicity, we focus on one-dimensional (1D) systems, for which powerful numerical techniques are available in terms of matrix-product states (MPS) [19–21]. We argue that it does not suffice to study only the optical conductivity, since the pump as well as the probe pulse can induce currents, which can modify the low-frequency behavior, without being a direct proof for SC. Nevertheless, we are able to provide evidence for the emergence of SC in the course of time by studying the time evolution of spectral functions, which are accessible to variants of time- and angle-resolved photoemission spectroscopy (tr-ARPES) experiments [22–28]. We propose to study the usual single-particle and a pairing spectral function, which we introduce below. We find particularly in the latter quantity clear signatures for the accumulation of weight at $k = 0$, indicative for the (quasi-)condensation of pairs, realizing a transient SC state with quasi-long-range order (qLRO). While our results indicate the persistence of qLRO, non-equilibrium situations can be beyond the realm of validity of the Mermin-Wagner-Hohenberg theorem [29–31], which inhibits the formation of true long-range order (LRO) in 1D systems. The scope of this Letter is, therefore, three-fold: To demonstrate that the time evolution of the optical conductivity does not suffice to unambiguously establish transient SC order, to present spectral functions as a more reliable probe, and to test the possible realization of LRO in 1D out-of-equilibrium systems by investigating correlation matrices. The general validity of our findings is supported by comparing the extended Hubbard model [32–38] and a variant of the 1D $t$-$J$ model [3, 39–44].

Model and methods  We study the time evolution of Hubbard chains [45–48] following a quantum quench [49]. Recent experiments [7–9, 11] on high-$T_c$ superconductors suggest that if there are preformed double occupancies, e.g., in the normal state slightly above $T_c$, pumping particular phonon modes induces charge coherences, which drive the system into a transient superconducting state. Therefore, our starting point is to assume that lattice distortions modify the strength of the couplings [10, 13] and thereby alter the nearest-neighbor interaction between the electrons, so that we consider a quench in the 1D extended Hubbard model,

$$\hat{H} = \hat{T} + U \sum_j \hat{n}_{j,\uparrow} \hat{n}_{j,\downarrow} + V \sum_j \hat{n}_j \hat{n}_{j+1}$$

(1)
with \( \hat{T} = -t_{\text{hop}} \sum_{j,\sigma} \left( \hat{c}_{j,\sigma} \hat{c}_{j+1,\sigma}^{\dagger} + \text{h.c.} \right) \) being the kinetic energy. Therein, \( \hat{c}_{j,\sigma}^{(t)} \) are \( S^{-1/2} \) fermionic ladder operators, which obey the canonical anticommutation relations \( \{ \hat{c}_{i,\sigma}, \hat{c}_{j,\sigma}^{\dagger} \} = \delta_{i,j} \delta_{\sigma,\sigma'}, \{ \hat{c}_{i,\sigma}, \hat{c}_{j,\sigma'} \} = \{ \hat{c}_{i,\sigma}, \hat{c}_{j,\sigma'} \} = 0 \), and we denote by \( n_j = \hat{n}_{j,\uparrow} + \hat{n}_{j,\downarrow} \) the total electron occupation at site \( j \). For later convenience, we also define doublon ladder operators \( \hat{d}_{j,\sigma}^{(t)} \equiv \hat{c}_{j,\sigma}^{\dagger} \hat{c}_{j,\sigma} \). As motivated above, we start in a charge-density wave (CDW), which favors double occupancies \( (U/t) \). We perform a sudden quench in the nearest-neighbor interaction \( V(t_{\text{hop}} = 1/4) \) \cite{17, 50}. We then calculate the real-time evolution using a combined single- and two-site time-dependent variational principle (TDVP) scheme in the MPS formulation of the density-matrix renormalization group (DMRG) for lattices \cite{19–21, 52} with up to \( L = 80 \) sites, open boundary conditions, and a maximal bond dimension of \( m_{\text{max}} = 1000 \) states. To investigate the formation and stability of transient SC, we studied the differential optical conductivity after a probe pulse \cite{53, 54}, spectral functions, and the correlation matrices \cite{55, 56} of single- and two-particle excitations \cite{22–27, 57–59}. We complement our studies by considering a similar quench in the 1D \( t-J_{\downarrow} \) model \cite{43, 44}, \( H_{t-J_{\downarrow}} = \hat{T} + J_{\downarrow}/2 \sum_j \left( \hat{S}_{j}^{\uparrow} \hat{S}_{j+1}^{\downarrow} + \hat{S}_{j}^{\downarrow} \hat{S}_{j+1}^{\uparrow} \right) \), at filling \( n = 0.2 \) by quenching \( J_{\downarrow}/t_{\text{hop}} = 2 \rightarrow 6 \), i.e., from a Luttinger liquid \cite{60} to a singlet SC phase \cite{61}. We choose our energy and time units by setting \( t_{\text{hop}} \equiv 1 \) and \( \hbar \equiv 1 \).

**Time-dependent Optical Conductivity** The experimental setups \cite{7–9, 11} we refer to typically measure the reflectivity after pump-probe excitations, from which the optical conductivity is extracted. We follow Refs. \( 53 \) and \( 54 \) and compute the differential optical conductivity

\[
\sigma(\omega, \Delta t) = \frac{j(\omega, \Delta t)}{i(\omega + i\eta)A(\omega, \Delta t)E} \equiv \sigma_1(\omega, \Delta t) + i\sigma_2(\omega, \Delta t)
\]

(2)
after the quench at \( t = 0 \). \( A(\omega, \Delta t) \) is the vector potential of the Fourier-transformed Gaussian probe pulse \( A(t, \Delta t) = A_0 e^{-\frac{(t-t_0)^2}{2\Delta_t^2}} \cos(\omega t_0) \) in Peierls substitution \cite{62} applied after the time delay \( \Delta t \). The response current \( j(t, \Delta t) = i \sum_{j,\sigma} \left( e^{-iA(t,\Delta t)\hat{c}_{j,\sigma}^{\dagger} \hat{c}_{j+1,\sigma} + \text{h.c.}} \right) \) was calculated from a real-time evolution of the perturbed system, and the \( \omega \)-dependence \( j(\omega, \Delta t) \) is obtained by a Fourier transform \cite{63}. We show the real (Fig. 1a) and imaginary (Fig. 1b) parts of \( \sigma(\omega, \Delta t) \) for delays up to \( \Delta t = 10 \) and a system with \( L = 64 \) sites. For the real part, we find a sudden transfer of spectral weight from the CDW signal at around \( \omega \approx 3 \) towards \( \omega \approx 1.7 \), which is due to the sudden change of the Hamiltonian. This insinuates that quasi-particles with twice the mass are seen in the response function, since their energy is (about) half of the original one \cite{43}. At the same time, in the imaginary part a peak forms near \( \omega = 0 \). We compare this to the SC ground state and realize that, at the first glance, similar behavior is induced. However, in particular in \( \sigma_1 \), clear differences appear, and \( \sigma_2 \) shows additional features. Also, it is hard to decide whether \( \sigma_2(\omega, \Delta t) \) is diverging as \( 1/\omega \) for \( \omega \rightarrow 0 \), since we are limited in the frequency resolution. We conclude

![FIG. 1](image-url)

Real (a) and imaginary (b) part of the optical conductivity \( \sigma_{1,2}(\omega, \Delta t) \) with probe pulses applied at different time delays \( \Delta t \). The Bottom panel (c) shows the real-time evolution of the response current \( j(t - \Delta t, \Delta t) \) after application of a probe pulse at time delay \( \Delta t \) following the quench (green) and in the SC ground state (orange). The charge flow after applying the probe pulse in the SC phase is shown in the inset.
that, as in the experiments, the question whether the accumulation of spectral weight near $\omega = 0$ is due to induced SC or an enhanced metallicity after a pump pulse is hard to decide. However, in contrast to the experimental situation we have direct access to the time dependence of the current induced by the probe pulse. The properties of this current are further illustrated by the inset of Fig. 1c, where we display the response electron density $\langle \hat{n}_i(t) \rangle_{\text{probe}} - \langle \hat{n}_i(t) \rangle_0$, which compares the time evolution of the local density in the SC phase with and without probe pulse. As can be seen, the effect of the probe pulse is to accumulate charge at the edges of the system. After passage of the probe pulse, this causes the measured current. In the SC phase the probe pulse induces a long-living DC current, while in non-equilibrium we find no clear evidence for a comparable response (see Fig. 1c). In turn, in our simulations the induced charge flow decays on time scales of at least $t \sim 25/t_{\text{hop}}$ which sets the scale of a low-frequency response $2\pi/t \approx 0.25$ in the imaginary part $\sigma_2$. Thus, a strengthening of the response at $\omega \to 0$ alone, as observed here, does not suffice to demonstrate SC.

**Spectral Functions** From now on we consider postquench states at $\Delta t = 15/t_{\text{hop}}$. This is justified, since for times $t > 4/t_{\text{hop}}$ a transient state is reached, as seen in the time evolution of the eigenvalues of the correlation matrix (see below), which we find to be non-thermal [51]. Motivated by tr-ARPES, we consider the in- and out-of-equilibrium time-dependent lesser Greens functions for $t > \Delta t$: $C_O(j, t, \Delta t) = \langle \psi(\Delta t) | \hat{O}_j(t) \hat{O}_{-\pi/2}^{\dagger}(0) | \psi(\Delta t) \rangle$ in the single- and two-particle channel, i.e., $\hat{O}_j = \hat{c}_{j,\uparrow}$ and $\hat{O}_j = \hat{d}_j$, respectively, and we indicate the equilibrium case by setting $\Delta t \equiv 0$. We refer to the Fourier transform to momentum and frequency space [51]

$$S_O(q, \omega, \Delta t) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} \sum_j e^{-i(qr_j - (\omega + i\eta)t)} C_O(j, t, \Delta t),$$  

(3)

as the differential spectral function, which we have introduced a spectral broadening $\eta > 0$ [21]. Note that here we explicitly do not restrict ourselves to single-electron excitations, but also study processes that may excite double occupations, i.e., doublons. This can be related to ongoing experiments [58], in which photoemission of pairs of electrons is studied, and theoretically underdetermined in a BCS-type picture [57]. Fig. 2 displays the spectral functions for double occupations $S_d(q, \omega, \Delta t)$ for both equilibrium phases (SC and CDW) and after the quench. We obtain a clear accumulation of weight at $q = 0$ in the postquench state, which renders the result similar to the one of the SC ground state displayed. This is the central statement of this Letter: A (quasi-)condensate of s-wave (Cooper-)pairs forms after the quench, which is clearly detectable in $S_d(q, \omega, \Delta t)$. We emphasize that this coherence between the changes is dynamically created after the quench, as seen in the comparison with Fig. 2b, which shows dispersive, incoherent doublons. In summary, spectral weight is shifted due to the quench from the dispersive band in the CDW ground state towards $q = 0$, indicating the formation of a (quasi-)condensate of bosonic quasi-particles, with a striking similarity to the spectral function in the SC ground state. We observe similar behavior in the corresponding pairing spectral function of the $t-J_L$ model [51], so that we expect this to be a generic feature, at least for quenches to SC phases.

Current tr-ARPES experiments usually investigate the time evolution of the spectral functions for single-electron excitations $S_C(q, \omega, \Delta t)$, which we show in Fig. 3. The signatures to discriminate the SC phase from the CDW phase are not as prominent as for the double occupations. Nevertheless, we find that in the SC ground state (Fig. 3a) there is a shift of spectral weight towards $q = \pi/2$. This is to be contrasted with the distribution of weights in the CDW ground state, where the maximum value is at $q = 0$, while in the SC ground state the maximum value of the spectral function is in the lower branch at $q \approx \pi/2$. Comparing to the spectral function after the quench (Fig. 3c), a weak transfer of spectral weight from $q = 0$ towards $q = \pi/2$ can be identified. However, from the numerical data it is not possible to clearly identify this as a signal for a (transient) SC phase.

**Correlation matrices** Now we turn to the question whether there is true LRO forming after the quench. In Ref. 55, Onsager and Penrose suggest to detect off-diagonal LRO by determining the eigenvalues $\lambda_\nu$ of correlation
FIG. 3. Spectral functions of single-particle excitations in equilibrium SC phase (a), CDW phase (b), and in non-equilibrium after quenching from CDW ground state into SC phase evaluated at times $t > 15$ (c).

matrices

$$
\chi_\varphi = \sum_{i,j} e_i \langle \hat{\varphi}_i^\dagger \varphi_j | \psi \rangle e_j = \sum_{i,j} e_i \chi_\varphi (i,j) e_j^\dagger ,
$$

i.e., $\chi_\varphi v_\beta = \lambda_\beta v_\beta$. The correlation matrix determines the order parameter if the dominating eigenvalue scales extensively in the system size $\lim_{L \to \infty} \frac{\lambda}{L} \to O(1)$, which also implies an extensive separation of the dominating eigenvalue $\lambda_L$ from the bulk [51].

Due to the Mermin-Wagner-Hohenberg theorem [29–31], in 1D and in equilibrium, for pair formation only qLRO can be realized, which translates to a SC order parameter vanishing in the thermodynamic limit. In order to test this in a non-equilibrium setup, we studied the time evolution of the correlation matrix $\chi_\varphi (i,j) = \langle \psi(t) | \hat{\varphi}_i^\dagger \hat{\varphi}_j | \psi(t) \rangle$, which provides the SC order parameter. Figure 4 shows the difference between the two largest eigenvalues $\Delta \lambda / L = \frac{\lambda_{L} - \lambda_{L-1}}{L}$, which exhibits a consistent separation of more than one order of magnitude during the time evolution. We have estimated the saturation values of the dominating eigenvalue by averaging over the accessible time scales, in which we assumed quasi-stationarity, $\lambda_L = \frac{1}{t_1 - t_0} \sum_{t=t_0}^{t=t_1} \lambda_L (t)$ with $t_0 = 10, t_1 = 32$. In the inset of Fig. 4, we compare the scaling behavior to the one of the SC ground state, where $\beta_{SC} \equiv \lambda_{SC} / L \sim L^{-0.50}$ is realized, with saturation value $\beta_{SC} = -1 \times 10^{-3} \approx 0$, as expected. After the quench, the scaling is best described by fitting the asymptotic behavior with $\lambda_{L} / L \sim L^{-0.92} \sim 1/L$, and in this case we extracted a value $\beta = 9 \times 10^{-4}$, whose magnitude is even smaller than the one obtained in equilibrium, and hence zero within the error bars of our scaling analysis. This scaling to zero indicates that no true LRO is obtained on the time scales investigated but cannot be excluded for later times [64, 65].

**Conclusion and Outlook** Our results for the differential optical conductivity in the extended Hubbard model after a quench indicate that the enhancement of $\sigma_2 (\omega, \Delta t)$ in the low-frequency regime does not suffice to uniquely identify SC: The currents induced by a probe pulse cannot unambiguously be identified as supercurrents. In contrast, the pairing spectral function shows a clear accumulation of weights at $q \to 0$, which is absent in our initial state, but present in the SC ground state. This provides stronger evidence for the formation of a SC state than the reflectivity measurements. The scaling to zero of the largest eigenvalue of the pairing correlation matrix shows that this transient state on the time scales investigated does not carry SC LRO. This opens the theoretical question whether this is only true for the non-equilibrium dynamics of 1D systems, or if the different scaling behavior indicates the possibility that in higher dimensions true SC LRO could be realized out-of-equilibrium. We expect that the pairing spectral function can also be used as strong indicator for SC in these setups.

In summary, our study indicates that reflectivity measurements need to be complemented by tr-ARPES-type experiments in future investigations. Readily available tr-ARPES setups measure the single-particle spectral function, which shows a shift of weights towards the SC state. We propose to also investigate the time evolution of pairing spectral functions, which provide the clearest evidence for the formation of a transient SC state.
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[43] A. V. Gorshkov, S. R. Manmana, G. Chen, J. Ye, E. Demler, M. D. Lukin, and A. M. Rey, Phys. Rev. Lett. 107, 115301 (2011).

[44] S. R. Manmana, M. Möller, R. Gezzi, and K. R. A. Hazzard, Phys. Rev. A 96, 043618 (2017).

[45] J. Hubbard, Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 276, 238 (1963).

[46] M. C. Gutzwiller, Phys. Rev. Lett. 10, 159 (1963).

[47] J. Kanamori, Progress of Theoretical Physics 30, 275 (1963).

[48] F. H. L. Essler, H. Frahm, F. Göhmann, A. Klümper, and V. E. Korepin, The One-Dimensional Hubbard Model (Cambridge University Press, Cambridge, 2005).

[49] J. Eisert, M. Friesdorf, and C. Gogolin, Nature Physics 11, 124 (2015).

[50] N. Bittner, “Novel nonequilibrium dynamics in superconductors: Induced superconductivity and higgs modes,” PhD thesis, Freie Universität Berlin, 2017.

[51] See Supplemental Material at [URL will be inserted by publisher] for a detailed description of the definition and numerical details of the spectral functions, (non-)thermal properties of the postquench state, scaling analysis of the eigenvalues of the correlation matrices (natural orbitals), and results for the $t-J_\perp$ model.

[52] J. Haegeman, C. Lubich, I. Oseledets, B. Vandereycken, and F. Verstraete, Phys. Rev. B 94, 165116 (2016).

[53] Z. Lenarčič, D. Golež, J. Bonča, and P. Prelovšek, Phys. Rev. B 89, 125123 (2014).

[54] C. Shao, T. Tohyama, H.-G. Luo, and H. Lu, Phys. Rev. B 93, 195144 (2016).

[55] O. Penrose and L. Onsager, Phys. Rev. 104, 576 (1956).

[56] M. Rigol and A. Muramatsu, Phys. Rev. A 70, 031603 (2004).

[57] K. A. Kouzakov and J. Berakdar, Phys. Rev. Lett. 91, 257007 (2003).

[58] A. Trützschler, M. Huth, C.-T. Chiang, R. Kamrla, F. O. Schumann, J. Kirschner, and W. Widdra, Phys. Rev. Lett. 118, 136401 (2017).

[59] C. Stahl and M. Eckstein, Phys. Rev. B 99, 241111 (2019).

[60] T. Giamarchi, Quantum Physics in One Dimension, International Series of Monographs on Physics, Vol. 121 (Oxford University Press, Oxford, 2004).

[61] The operators $S^z_j$ are the usual $S - \frac{1}{2}$ ladder operators on site $j$. Note that double occupancies are forbidden in the $t-J$ model.

[62] D. R. Hofstadter, Phys. Rev. B 14, 2239 (1976).

[63] In [54] the non-equilibrium response function is obtained by considering the Fourier transform of the difference $j(t, \Delta t) - j_0(t)$ with $j_0(t)$ the current without probe pulse. As in our quench protocol without probe pulse there is always $j_0(t) \equiv 0$ we drop this term for brevity.

[64] Y. Lemonik and A. Mitra, Phys. Rev. B 96, 104506 (2017).

[65] V. Lemonik and A. Mitra, Phys. Rev. Lett. 121, 067001 (2018).
SPECTRAL FUNCTION

We defined the differential spectral function $S_{\hat{O}}(q, \omega, \Delta t)$ by the power spectrum in momentum space of the propagator of the operators $\hat{O}_j$

$$S_{\hat{O}}(q, \omega, \Delta t) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} C_{\hat{O}}(q, t, \Delta t) ,$$

$$C_{\hat{O}}(q, t, \Delta t) = \frac{1}{L} \sum_{r_{ij}} e^{-iqr_{ij}} \langle \psi(\Delta t)|\hat{O}_i(t)\hat{O}_j(0)|\psi(\Delta t)\rangle = \langle \hat{O}_i(t)\hat{O}_j(0) \rangle_{\Delta t} ,$$

where we assumed a (quasi-)steady state to exploit time translational invariance to shift the argument: $\langle \hat{O}_i(-t)\hat{O}_j(0) \rangle = \langle \hat{O}_i\hat{O}_j(0) \rangle$. Thus, we can evaluate the time integral by taking the real part of the Fourier transformation and restrict the integration domain to $t \geq 0$. Note that in order to discretize the Fourier transformation, we defined the limit as

$$S_{\hat{O}}(q, \omega, \Delta t) = \lim_{T \to \infty} \frac{1}{T} \int_{-T/2}^{T/2} dt e^{i\omega t} C_{\hat{O}}(q, t, \Delta t) .$$

Using Eq. (4), we thus numerically evaluated the Fourier transformation via

$$S_{\hat{O}}(q, \omega_n, \Delta t) = \frac{\delta}{T} \text{Re} \sum_{m=0}^{N_T-1} e^{i\omega_nt_m} C_{\hat{O}}(q, t_m, \Delta t) ,$$

with discretized frequencies $\omega_n = \frac{2\pi}{T} (n = 0, \ldots, N_T - 1)$, $t_m = m\delta$ and the summation range fixed by the time step $\delta = T/N_T$. Note, that this way we only obtain the positive frequency part which we accounted for by shifting the time arguments, relabeling $t_m \to t_m - T/2 \Rightarrow \omega_n \to \omega_n - \pi/T$.

Furthermore, integrating over the frequency domain, the propagator fulfills

$$\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} C_{\hat{O}}(q, t, \Delta t) = \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} \sum_{n,m} \langle \psi(t)|n\rangle \langle n|\hat{O}_i(t)|m\rangle \langle m|\hat{O}_j\psi(\Delta t) \rangle = \langle \hat{O}_i\hat{O}_j \rangle_{\Delta t} ,$$

which implies the sum rule

$$2 \sum_q \int_{-\infty}^{\infty} d\omega \text{Re} S_{\hat{O}}(q, \omega, \Delta t) = \sum_q \langle \hat{O}_i\hat{O}_j \rangle_{\Delta t} .$$

Thus, for $\hat{O}_i = \delta_{i,\sigma}$ this yields the total number of particles with local spin projection $\sigma$, while for $\hat{O}_i = \delta_i$ we expect the overall number of doublons in the system.
Note that the overall doublon occupation \( \hat{D} = \sum_i \hat{d}_i^\dagger \hat{d}_i \) in general is not conserved by \( \hat{H} \). However, the sum rule holds at each time delay \( \Delta t \). In particular, if the correlation function is invariant under time-translations on some time interval \( I \), \( \hat{D} \) will be conserved on \( I \).

**NATURAL ORBITALS**

**General Theory** We consider a correlation matrix for some local observable \( \hat{O}_j \)

\[
\chi_{\hat{O}}(i,j) = \langle \psi | \hat{O}^\dagger_j \hat{O}_j | \psi \rangle .
\]  

Then, off-diagonal long-range order (LRO) in the thermodynamic limit is defined according to

\[
\lim_{|i-j| \to \infty} \chi_{\hat{O}}(i,j) > 0 ,
\]

i.e., the correlation function \( \chi_{\hat{O}}(i,j) \) saturates at a finite value for arbitrary large separations \( |i-j| \). In the following we will briefly summarize the discussion on natural orbitals (see, for instance, \([1,2]\)) to review the tools exploited in the main text to identify off-diagonal LRO.

For a finite system with \( L \) lattice sites, \( \chi_{\hat{O}}(i,j) \) is a Hermitian \( L \times L \) matrix, which we can formally diagonalize to obtain real eigenvalues \( \lambda_\nu \) and corresponding eigenvectors \( v_\nu \). Expanding \( \chi_{\hat{O}}(i,j) \) as matrix \( \chi_{\hat{O}} \) in its eigenbasis, we can write

\[
\chi_{\hat{O}} = \sum_\nu v_\nu \langle \psi | \left( \sum_i v_\nu,i \hat{O}_i^\dagger \right) \left( \sum_j v_\nu,j \hat{O}_j \right) | \psi \rangle v_\nu^\dagger .
\]

Introducing field operators \( \hat{\eta}_\nu = \sum_i v_\nu,i \hat{O}_i \), their squared expectation values are related to the eigenvalues \( \lambda_\nu \) of \( \chi_{\hat{O}} \)

\[
v_\nu \chi_{\hat{O}} v_\nu = \langle \psi | \hat{\eta}_\nu^\dagger \hat{\eta}_\nu | \psi \rangle = \lambda_\nu \geq 0 ,
\]

i.e., the eigenvalues are strictly positive. If we impose

\[
\left[ \hat{O}_i, \hat{O}_j^\dagger \right] = \delta_{ij} \text{ with } \epsilon = \pm 1 \text{ choosing between the commutator (+1) and anticommutator (−1), it follows that}
\]

\[
\left[ \hat{\eta}_\nu, \hat{\eta}_\mu^\dagger \right] = \sum_{i,j} \left[ \hat{O}_i, \hat{O}_j^\dagger \right] \delta_{\nu,i} v_{\mu,j}^* = \delta_{\nu\mu} .
\]

This suggests to call the eigenvectors \( v_\nu \) natural orbitals and the eigenvalues natural orbital occupations \( \lambda_\nu \) of the correlation matrix \( \chi_{\hat{O}} \).

The existence of off-diagonal LRO can now be related to properties of the natural orbitals. To see this note, that due to the canonical commutator relations of \( \hat{O}_j \) the trace over \( \chi_{\hat{O}} \) corresponds to the total occupation

\[
N_{\hat{O}} = \sum_j \langle \hat{n}_j \rangle = \sum_j \langle \hat{O}_j^\dagger \hat{O}_j \rangle \text{ of the single particle states generated by the } \hat{O}_j \text{'s. If we assume, that there is a natural orbital } v_L \text{ which is macroscopically occupied, i.e., } \lambda_L/N_L \sim O(1), \text{ it is instructive to pull out this contribution from the sum in Eq. (11). Written out component-wise, we find}
\]

\[
\chi_{\hat{O}}(i,j) = \lambda_L v_{L,i} v_{L,j}^\dagger + \sum_{\nu < L} \lambda_\nu v_{\nu,i} v_{\nu,j}^\dagger .
\]

The natural orbitals are normalized so that in general the components fulfill \( v_{\nu,j} \sim 1/\sqrt{L} \). Therefore, an extensively scaling natural orbital occupation \( \lambda_L \) yields a dominating leading summand in the above expansion of the correlation matrix while the remaining summands are suppressed as \( 1/L \). In this situation, for increasing system sizes \( L \) the correlation matrix is well approximated by neglecting the latter

\[
\chi_{\hat{O}}(i,j) = \lambda_L v_{L,i} v_{L,j}^\dagger + O(1/L) \approx \lambda_L v_{L,i} v_{L,j}^\dagger .
\]

The correlation matrix obtained this way factorizes in the spatial components \( (i,j) \). Since, in a state with explicitly broken symmetry with respect to \( \hat{O}_j \), one expects \( \langle \hat{O}_j \rangle \neq 0 \), which permits to identify

\[
\chi_{\hat{O}}(i,j) = \langle \hat{O}_i^\dagger \rangle \langle \hat{O}_j \rangle \equiv \sqrt{\lambda_L} v_{L,i} \sqrt{\lambda_L} v_{L,j}^\dagger ,
\]

so that \( \sqrt{\lambda_L} v_{L,i} \) constitutes the microscopic order parameter.

**Quasi-long-range order and error estimates** In the following paragraphs, we focus on our results for the correlation matrix of double occupancies \( \chi_{\hat{d}}(i,j) = \langle \psi | \hat{d}_i^\dagger \hat{d}_j | \psi \rangle \). The problem under consideration is one-dimensional so that due to the Mermin-Wagner-Hohenberg theorem \([3-5]\) at least in the ground state there can be quasi-long-range order (qLRO), only. This translates to a still extensively scaling, dominating natural orbital but with vanishing value in the thermodynamic limit. In the case of a non-interacting gas of hard-core bosons on a lattice, it is well-known \([6,7]\) that

\[
\frac{\lambda_0}{L} \sim \frac{A}{\sqrt{L}} + \beta
\]

with \( \beta \equiv 0 \), which in excellent agreement with our ground-state calculations in the superconducting phase at \( U = -4, V = -1/4 \) and \( \hat{O}_j = \hat{d}_j \). We performed a finite size scaling of the eigenvalue of the dominant natural orbital by fitting the function \( \lambda_0 \) over \( L^{-\gamma} \) with \( \gamma = 0.50 \) in the superconducting ground state. The obtained value for the order parameter is \( \beta = -1 \times 10^{-3} \), which we used to gauge the precision of our method to \( \delta \sim O(10^{-3}) \).

In the non-equilibrium situation, we time-averaged the dominating natural orbital for times \( t_0 \geq t_0 \) via

\[
\bar{\lambda}_0 = \frac{1}{t_1 - t_0} \sum_{n} \lambda_0 (t_0 + n \delta) ,
\]
with $\delta$ being the time step of the time-evolution scheme and with $t_0 = 10, t_1 = 32$. Performing the finite-size analysis, we found the data to be best described by a scaling $\sim \alpha \cdot L^{-\gamma} + \beta$ with $\gamma = 0.92$ and $\beta = 9 \cdot 10^{-4}$. Within the error bounds deduced from the ground-state analysis, this implies $\beta \equiv 0$, and hence no LRO.

**Momentum space** To complete the discussion, we calculated the Fourier transformation of the natural orbitals $\tilde{v}_\nu = \sum_{ij} v_{\nu,j} e^{iqj}$. As shown in Fig. 1, the Fourier modes $\tilde{v}_\nu$ are nearly diagonal in $k$-space, i.e., the correlation matrix is approximately diagonalized by a Fourier transformation and the dominating natural orbital (NO) is characterized by a mode with $q = 0$. The off-diagonal contributions around $q = \pi$ arise from highly excited states (c.f. the band spectral function in the main text). Inspecting their real-space distributions $|v_{\nu,j}|^2$ (not shown here) these are located near the boundaries so that we conjecture them to vanish in the thermodynamic limit. We observe these properties consistently for times $t > 4$ in all considered system sizes $L \in [32, 80]$.

**J-QUENCH IN THE t-J⊥ CHAIN**

Next to the extended Hubbard model, we considered the quench dynamics of the one-dimensional $t$-$J_\perp$ Hamiltonian [8, 9]

$$\hat{H}_{t-J_\perp} = -t_{\text{hop}} \sum_{j,\sigma} \left( \hat{c}_{j,\sigma}^\dagger \hat{c}_{j+1,\sigma} + \text{H. c.} \right)$$

$$+ J_\perp \sum_{j} \left( \hat{S}_{j}^+ \hat{S}_{j+1}^- + \hat{S}_{j}^- \hat{S}_{j+1}^+ \right),$$

at filling $n = 0.2$. Its phase diagram [9] at $n = 0.2$ features a metallic (Luttinger liquid [10]) spin-density wave phase (SDW) at $J_\perp = 2t_{\text{hop}}$ and a spin-gapped singlet SC phase at $J_\perp = 6t_{\text{hop}}$. In the following, we compute the equilibrium one-particle as well as singlet-pair spectral functions at these two points in parameter space and also the non-equilibrium spectral functions at late times for a quench $J_\perp = 2t_{\text{hop}} \rightarrow J_\perp = 6t_{\text{hop}}$. Furthermore, we discuss the time-evolution of the natural orbital occupations.

**Spectral functions** We consider the singlet-pair creation and annihilation operators

$$\Delta_{j_1}^{(t)} = \frac{1}{\sqrt{2}} \left( \hat{c}_{j_1,\uparrow} \hat{c}_{j_1,\downarrow} - \hat{c}_{j_1,\uparrow}^\dagger \hat{c}_{j_1,\downarrow}^\dagger \right)$$

and compute the two-particle spectral function according to Eqs. (1) and (6). The results are shown in Fig. 2 for the singlet-pair spectral function. The quasi-stationary state is estimated to be reached after about 20 time units. This is estimated from the time-evolution of the natural orbitals (cf. the corresponding section below).

The equilibrium two-particle SC spectral function shows a large weight at $q = 0$, whereas in the spin-density wave state it is much lower and a dispersion is visible. The peak amplitude of the non-equilibrium state is about doubled in comparison to the SDW and shifted towards the SC peak position. This is consistent with our findings in the extended Hubbard model in the main text where we find an increase of spectral weight around $q = 0$ in the postquench state (see Fig. 2c) and a shift of weight towards the SC state.
In the single-particle case the equilibrium spectral functions show the occupied states of a cosine dispersion (the unoccupied part of the spectrum is seen in the spectral function obtained from the greater Green’s function). The spectral weights are of comparable amplitude but clearly differ in their \( \omega \)-axis position. The non-equilibrium state is a kind of hybrid that contains weight around both the equilibrium branches.

Shift of the spectral peak As a guide to the eye, the peaks of the one- and two-particle spectral functions are replotted in Fig. 4. In addition to a slight increase in weight one can clearly see that the two-particle spectral peak in the post-quench state has shifted towards the superconducting peak position whereas in the one-particle case the picture is more complicated.

Hence, like in the main text the two-particle spectral function seems to be a more reliable indicator for the formation of transient superconducting spectral weights.

Natural orbitals At the end, analogous to the main text, we consider the question of whether true long-ranged order out-of-equilibrium is detectable from the correlation matrices. In Fig. 5 the time-dependent largest eigenvalue of the singlet-pair correlation matrix \( (\Delta^\dagger \Delta)_t \) is shown. As for the extended Hubbard model in the main text a saturation value can be made out after 20 time units. We use this as the criterion for the choice of the nonequilibrium reference state.

In order to perform a scaling analysis \( \lambda_m/L = \alpha \cdot L^{-\gamma+\beta} \), we average over all largest natural orbitals for times \( 20 \leq t \leq 30 \). The results shown in the inset of Fig. 5 yield a value of \( \beta \approx -6 \cdot 10^{-5} \), such that \( \beta \approx 0 \) within the estimated error bounds. This supports the conclusion that no true long-ranged order is realized in the transient state also for this model. The scaling exponent is found to be \( \gamma \approx 1.12 \) which is somewhat close to the scaling exponent of 0.92 found in the extended Hubbard model. Note, that by definition \( \gamma \leq 1 \) so that the obtained scaling exponent has an error of \( \approx 10\% \).

COMPARISON TO FINITE TEMPERATURE STATES

All our simulations were performed on pure states that are either ground-states of the models under consideration or quenches from the latter. The question arises whether, following the quench, the system reaches a state in which local observables are thermalized towards their values in the canonical ensemble. To address this issue, we calculated the density matrix \( \hat{\rho}(\beta) \) in the SC phase where we choose the inverse temperature \( \beta = 1/T \) in a way that \( \langle \hat{H} \rangle_{\beta Q} = \langle H \rangle_\theta \). Here, \( \langle \cdots \rangle_\theta \) denotes the expectation value of \( \hat{H} \) after the quench and \( \langle \cdots \rangle_\beta \) is the
FIG. 5. Time evolution of the largest natural orbital for the quench in the $t$-$J_\perp$ model; the transient state is reached after about 20 time units. Inset: extrapolated scaling of the dominating natural orbital with the system size.

FIG. 6. Energy $\langle \hat{H} \rangle_\beta$ during imaginary time evolution of a system with $L = 32$ sites over imaginary time $\beta$. The inset shows the superconducting correlation function $P_1(L/2)$ during the time evolution after a global quench from the CDW to the SC phase at time step $t = 10$ (green), and in a thermal state with $\langle \hat{H} \rangle_\beta$ corresponding to the energy of the quenched system $E_{\text{quench}}$ (purple).

In both the thermal state and the quenched state at $t = 10$ in the inset of Fig. 6. As can be seen, we do not obtain a state that is characterized by a thermal density matrix with inverse temperature $\beta_Q$ chosen in a way such that its energy matches the one after the quench.

The expectation value of $\hat{H}$ with respect to a thermal state $\hat{\rho}(\beta)$ in the superconducting phase. In order to obtain the correct inverse temperature, we performed an imaginary time evolution on an infinite-temperature state $\hat{\rho}(0)$ and cooled down the system this way until the energy matched the one of the quenched state [11]. In Fig. 6, the obtained relation between energy and inverse temperature is displayed with the energy of the quenched state marked as dashed line. Having found the respective density matrix $\hat{\rho}(\beta_Q)$, we plot the expectation value of the superconducting correlation function

$$P_1(i, j) = e^{i\beta} \langle \hat{c}_{i, \uparrow} \hat{c}_{j, \downarrow} \hat{c}_{j, \uparrow} \hat{c}_{i, \downarrow} \rangle,$$

in both the thermal state and the quenched state at $t = 10$ in the inset of Fig. 6. As can be seen, we do not obtain a state that is characterized by a thermal density matrix with inverse temperature $\beta_Q$ chosen in a way such that its energy matches the one after the quench.

[1] O. Penrose and L. Onsager, Phys. Rev. 104, 576 (1956).
[2] I. Rousochatzakis, S. R. Manmana, A. M. Läuchli, B. Normand, and F. Mila, Phys. Rev. B 79, 214415 (2009).
[3] N. D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1133 (1966).
[4] N. D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1307 (1966).
[5] P. C. Hohenberg, Phys. Rev. 158, 383 (1967).
[6] M. Rigol and A. Muramatsu, Phys. Rev. A 70, 031603 (2004).
[7] M. Rigol and A. Muramatsu, Phys. Rev. A 72, 013604 (2005).
[8] A. V. Gorshkov, S. R. Manmana, G. Chen, J. Ye, E. Demler, M. D. Lukin, and A. M. Rey, Phys. Rev. Lett. 107, 115301 (2011).
[9] S. R. Manmana, M. Möller, R. Gezzi, and K. R. A. Hazzard, Phys. Rev. A 96, 043618 (2017).
[10] T. Giamarchi, Quantum Physics in One Dimension, International Series of Monographs on Physics, Vol. 121 (Oxford University Press, Oxford, 2004).
[11] S. Paeckel, T. Köhler, A. Swohoda, S. R. Manmana, U. Schollwöck, and C. Hubig, arXiv e-prints, arXiv:1901.05824 (2019), arXiv:1901.05824 [cond-mat.str-el].