Dynamical manifestation of Gibbs paradox after a quantum quench

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We study the propagation of entanglement after quantum quenches in the non-integrable paramagnetic quantum Ising spin chain. Tuning the parameters of the system, we observe a sudden increase in the entanglement production rate, which we show to be related to the appearance of new quasi-particle excitations in the post-quench spectrum. We argue that the phenomenon is the non-equilibrium version of the well-known Gibbs paradox related to mixing entropy and demonstrate that its characteristics fit the expectations derived from the quantum resolution of the paradox in systems with a non-trivial quasi-particle spectrum.

I. INTRODUCTION

A quantum quench is a protocol routinely engineered in cold-atom experiments [1–9]: a sudden change of the Hamiltonian of an isolated quantum system followed by a non-equilibrium time evolution. The initial state corresponds to a highly excited configuration of the post-quench Hamiltonian, acting as a source of quasi-particle excitations [10]. In a large class of systems, there is a maximum speed for these excitations called the Lieb-Robinson bound [11] which results in a linear growth of entanglement entropy $S(t) \sim t$ of a subsystem of length $\ell$ for times $t < \ell/2c_{\text{max}}$, after which it becomes saturated [12]. The mean entropy production rate $\overline{\sigma}, S$ characterizing the linear growth naturally depends on the post-quench spectrum and reflects its quasi-particle content.

Entanglement entropy contains a wealth of information regarding the non-equilibrium evolution and the stationary state resulting after a quench, and therefore has been studied extensively in recent years [13–20]. The growth of entanglement also has important implications for the efficiency of computer simulations of the time evolution [21–30]. Recently it has become possible to measure entanglement entropy and its temporal evolution in condensed matter systems [2, 31–32]. For integrable systems, an analytic approach of entanglement entropy production has been developed recently in [33–35].

In this paper we consider quenches in the quantum Ising chain by switching on an integrability breaking longitudinal magnetic field $h_x$ in the paramagnetic phase. In similar quenches in the ferromagnetic regime, it was recently found that confinement suppresses the usual linear growth of entanglement entropy and the corresponding light-cone-like spreading of correlations after the quantum quench [36]. However, in the paramagnetic regime considered here confinement is absent and thus entanglement entropy grows linearly in time. Nevertheless the dependence of the entropy production rate on the quench parameter $h_x$ shows another kind of anomalous behavior: a sudden increase setting in at the threshold value of $h_x$ where a new quasi-particle excitation appears in the spectrum.

Using the physical interpretation of the asymptotic entanglement of a large subsystem as the thermodynamic entropy of the stationary (equilibrium) state [36–37, 38], this can be recognized as arising from the contribution of mixing entropy between the particle species, and therefore constitutes a non-equilibrium manifestation of the Gibbs paradox.

II. ENTROPY PRODUCTION RATE AS A FUNCTION OF THE LONGITUDINAL FIELD

The Ising quantum spin chain is defined by the Hamiltonian

$$H = J \sum_{i=0}^{L-1} \left(-\sigma^x_i \sigma^x_{i+1} + h_z \sigma^z_i + h_x \sigma^x_i\right),$$

where $\sigma^{x,z}_i$ denote the standard Pauli matrices acting at site $i$, and we assume periodic boundary conditions $\sigma^{x,z}_0 = \sigma^{x,z}_L$. It is exactly solvable for $h_x = 0$ with a quantum critical point at $h_z = 1$. For $h_z < 1$, the system shows ferromagnetic ordering with order parameter $\sigma^z$. The paramagnetic phase corresponds to transverse magnetic field $h_z > 1$, where the spectrum consists of free fermionic excitations over a unique ground state with the dispersion relation

$$\epsilon(k_n) = 2J \sqrt{1 + h_x^2 - 2h_z \cos k_n},$$

$$k_n = \frac{n \pi}{L}, n = -\frac{L}{2}, -\frac{L}{2} + 1, -\frac{L}{2} + 2, \ldots, \frac{L}{2},$$

where we assumed that the chain length $L$ is even. The fermionic quasi-particles correspond to spin waves with the maximum propagation velocity of $\left(\frac{dk}{dk}\right)_{\text{max}} = 2J$

We consider quantum quenches in the thermodynamic limit $L \to \infty$. We prepare the system in the ground state

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The standard measure of the half-system entanglement is \[ S(t) = -\text{Tr} \rho_R(t) \log \rho_R(t) , \] which is just the von Neumann entropy of the reduced density matrix \( \rho_R(t) = \text{Tr}_L |\Psi(t)\rangle \langle \Psi(t)| \) of one half of the system obtained by tracing out the other half. The entropy production rate obtained from iTEBD simulations is shown in Fig. 1.

The top panel demonstrates that the average late time behavior of the entanglement entropy \( S(t) \) can be fit with a linear behavior apart from slowly decaying periodic fluctuations, as expected after a global quantum quench \[12\]. The mean entanglement production rate \( \partial_t S \) is obtained from the slope of the linear part and can be interpreted as the production rate of the thermodynamic entropy. In the bottom panel the dependence of \( \partial_t S \) on \( h_x \) is shown. After some initial increase the entropy production rate starts decreasing, but at some value of the lon-
The eigenvalue of $S$ is a complex phase $e^{ik}$ where $k$ is the momentum of the state, defined modulo $2\pi$.

A. The first quasi-particle excitation

From the numerically computed spectrum, the lowest-lying one-particle states can be selected as the lowest energy states among those with a fixed momentum $k \neq 0$, while at $k = 0$ the relevant state is the first excited above the ground state; this gives the first quasi-particle branch. The dispersion relation $\epsilon_1(k)$ of the first quasi-particle can be obtained by subtracting the ground state value, with the result shown in Fig. 2 for the case $h_z = 1.5$ and a few values of $h_x$. The data can be fitted to a very good precision with a curve of the form

$$\epsilon_1(k) = \sqrt{A + B \cos k},$$

inspired by the exact dispersion relation of the $h_x = 0$ chain. It is already apparent from the graph that the quasi-particle gap (mass) increases with $h_x$, while the Lieb-Robinson velocity

$$v_{\text{max}} = \max_k \frac{d\epsilon_1}{dk}$$

decreases, which can also be shown by computing $v_{\text{max}}$ numerically from the fit with the results shown in Table II.

A more complete picture of the properties of the first quasi-particle is shown in Fig. 3 for $h_z = 1.25$. This value was simply chosen for illustration; the qualitative picture does not change for other values for $h_z$. Note that the quasi-particle mass gets corrections of order $h_x^2$ for small $h_x$ and becomes linear for large $h_x$. The first one can easily be confirmed by perturbation theory, while the second is a simple consequence of the form of the Hamiltonian. Also note that the Lieb-Robinson velocity decreases with increasing $h_x$ and eventually goes to zero for very large $h_x$; this is easy to understand since for very large $h_x$ the dynamics of the spins essentially becomes frozen.

B. Bound states in the continuum limit

In the vicinity of the quantum critical point $h_z \sim 1$ and $h_x \sim 0$ it is possible to take a continuum limit to the scaling Ising field theory. For vanishing $h_x$ it describes a massive free Majorana fermion with mass $M = 2|J|/1-h_z$. For non-zero $h_x$, the coupling corresponding to $h_x$ in the

| $h_x$ | 1.25 | 1.5 | 1.75 | 2 |
|-----|-----|-----|-----|-----|
| $h_x^{\text{min}}$ | 0.040 | 0.140 | 0.268 | 0.412 |

Table I. Position of the local minimum of $\overline{\partial_h S}$ as a function of $h_x$ for different values of $h_x$.

| $h_x$ | 0.12 | 0.18 | 0.25 |
|-----|-----|-----|-----|
| $v_{\text{max}}$ | 1.873 | 1.772 | 1.657 |

Table II. Values of the Lieb-Robinson velocity determined from the data shown in Fig. 2.
continuum limit scales as \( h \propto h_x J^{15/8} \). The scaling limit is obtained by taking \( J \to \infty \) while \( h_x \to 0 \) such that

\[
M = 2J|1 - h_z|, \\
h = \frac{2}{s} J^{15/8} h_x, \quad \bar{s} = 2^{1/12} e^{-1/8} \mathcal{A}^{3/2} \\
\mathcal{A} = 1.282427129 \ldots
\]

are kept fixed, the quantum Ising spin chain scales to the Ising field theory given in terms of a Majorana fermion field \( \psi, \bar{\psi} \)

\[
H_{\text{IFT}} = \int_{-\infty}^{\infty} dx \left\{ \frac{1}{2\pi} \left( \frac{i}{2} \left( \psi(x) \partial_x \bar{\psi}(x) - \bar{\psi}(x) \partial_x \psi(x) \right) \\
- i M \bar{\psi}(x) \psi(x) \right) + h \sigma(x) \right\}, \\
\left\{ \psi(x, t), \bar{\psi}(y, t) \right\} = 2\pi \delta(x - y),
\]

using units in which the lattice spacing is \( a = 2/J \) and the resulting speed of light is \( c = 1 \). The operator \( \sigma(x) \) is the continuum limit of magnetization \( \sigma_x^z \) which is non-local with respect to the Majorana fermionic field and corresponds to a twist field changing the boundary condition of the fermion from periodic to anti-periodic and vice versa.

A detailed numerical study of the field theory limit revealed that switching on a longitudinal field \( h \) leads to the appearance of a second and a third quasi-particle excitation at some threshold values \( h_{z1} \) and \( h_{z2} \) which scale as \( M^{15/8} \). These excitations can be considered bound states of the fundamental one, and the spectrum only depends on the dimensionless ratio \( \chi = M/h^{8/15} \), with \( h = 0 \) corresponding to \( \chi = \infty \).

One can also approach the question of spectrum from the other extremum point \( \chi = 0 \), that is the case of \( M = 0 \) when one obtains the famous Ising model \([45]\). At this point there exist 8 particles with masses \( m_i \) in the continuum limit, the ratios of which are known exactly, with the first two having the values

\[
\Delta_{21} = \frac{m_2}{m_1} = 2 \cos \frac{\pi}{5} = 1.618 \ldots \\
\Delta_{31} = \frac{m_3}{m_1} = 2 \cos \frac{\pi}{30} = 1.989 \ldots
\]

As soon as one switches on a mass \( M \) which takes the system into the paramagnetic regime \([29]\) (corresponding to \( h_z > 1 \)), all but three of these particles become unstable \([44]\). Further increasing \( M \) (more precisely, the dimensionless ratio \( \chi \)) makes the third particle unstable in short order, with the second particle disappearing for much larger values of \( \chi \) \([44]\). For the limit of infinite \( \chi \) which corresponds to \( h = 0 \) i.e. a free massive Majorana fermion, only a single particle remains in the spectrum.

C. The bound state quasi-particles on the chain

Turning to the spin chain, now we demonstrate that the quasi-particle spectrum obtained in the scaling limit persists also for finite lattice spacing. For a fixed value of \( h_z \) there exists a threshold value \( h_x^{(2)} \) at which a new quasi-particle appears in the spectrum which can be identified as a bound state of the fundamental quasi-particle, as in the field theory. For values of \( h_z \) close enough to the critical point \( (h_z = 1) \) a third quasi-particle can also be found at sufficiently high \( h_x \) with a threshold value \( h_x^{(3)} \); however, this excitation is always very weakly bound.

The lowest branch of excitations discussed in Subsection IIIA correspond to the first quasi-particle, and for small enough \( h_x \) the excitations just above the first quasi-particle branch can be interpreted as two-particle states. However, for \( h_x > h_x^{(2)} \) the gap to the second branch drops below twice the value of the first quasi-particle gap, which signals the appearance of stable bound states forming a second quasi-particle branch. For even higher values \( h_x > h_x^{(3)} \) another branch drops below twice the first gap, signaling the presence of the third quasi-particle excitation in the spectrum.

\[\text{In fact, this is a little more complicated as the sign of mass term is irrelevant in the field theory. In the continuum limit, the distinction between the two phases is encoded in the Hilbert space, cf. Ref. [43].}\]
To find the bound state thresholds \( h_x^{(a)} (a = 2, 3) \) above which the new quasi-particles appear, we took the first four zero-momentum eigenvalues at chain length \( L \) ordered as \( E_0(L) < E_1(L) < E_2(L) < E_3(L) \), and computed the gap ratios

\[
\Delta_{21}(L) = \frac{E_2(L) - E_0(L)}{E_1(L) - E_0(L)} \quad \Delta_{31}(L) = \frac{E_3(L) - E_0(L)}{E_1(L) - E_0(L)},
\]

which were then extrapolated in \( L \) using

\[
\Delta_{a1}(L) = \Delta_{a1} + \gamma_{a1} e^{-\mu_{a1} L} \quad a = 2, 3.
\]

The condition for the existence of the bound states \( a = 2, 3 \) is that their decay is kinematically forbidden, i.e. \( \Delta_{a1} < 2 \), since the model is non-integrable and there are no conserved charges to prevent their decay.

The exponential volume dependence is expected to be valid when the bound state exists \([46]\), so the extrapolation was performed in the regime when \( h_x \) approaches the critical value \( h_x^{(a)} \) from above. The exponent \( \mu_{a1} \) is related to the spatial extension of the bound state wave function, while \( \gamma_{a1} \) is the interaction strength between the constituents which is negative as long as the bound state exists, i.e. above the critical value corresponding to an attractive interaction. Below the critical value, the energy level corresponds to a two-particle scattering state which is expected to have power-like leading finite size corrections \([47]\). Despite this, the numerical fit with the exponential dependence works quite well close to the threshold value \( h_x^{(a)} \) and confirms the change of the sign in \( \gamma_{a1} \) which corresponds to the interaction becoming repulsive.

For four different values of \( h_x = 1.25, 1.5, 1.75 \) and 2, the critical values \( h_x^{(a)} \) where a given bound state appears were found numerically from the condition \( \Delta_{a1} = 2 \) as illustrated in Fig. \([4]\). The critical values determined numerically are given in Table \([III]\).

| \( h_x \) | 1.25 | 1.5 | 1.75 | 2 |
|-----------|------|------|------|---|
| \( h_x^{(2)} \) | 0.040 | 0.146 | 0.261 | 0.400 |

Table \( III \). Critical values of \( h_x \) corresponding to the bound state threshold at some values of \( h_x \).

It is also clear from Fig. \([6]\) that the second quasi-particle mass depends more strongly on the chain length \( L \), especially when \( h_x \) is closer to the threshold value where the bound state appears. The reason is that the weaker the binding, the larger is the spatial extension of the two-body wave-function, therefore the more it is distorted in finite volume.

The numerical spectra of the spin chain show that the ratios \( \Delta_{a1} \) are consistently higher than the continuum \( E_8 \) values and increase with \( h_x \). As a result, the third particle can be observed only for the cases \( h_x = 1.25 \) and \( h_x = 1.5 \), where the critical values can be obtained in a similar way as for the second particle, and turn out to be \( h_x^{(3)} \approx 0.79 \) and \( h_x^{(3)} \approx 1.82 \). In addition, the third particle is extremely loosely bound for all values of \( h_x \) where it exists, and the numerical data suggest that it may eventually become unbound for much larger \( h_x \) although this is hard to nail down with sufficiently high precision due to finite size effects. This explains why there is no signature of the third particle in the entropy slope. Indeed, a quantum quench results in a “plasma” of finite energy density, which destabilizes any sufficiently loosely bound state by collisions with the particles present. One still expects some weak resonance in the spectral density of the two-particle continuum, though, and indeed hints of such a resonance state can be seen in the power spectra discussed in Section \([IV]\).

### D. Post-quench quasi-particle density

Finally, in Fig. \([7]\) we illustrate that the quenches we consider have very low quasi-particle density. The plots show the energy pumped into the quench, defined as the expectation value of the post-quench Hamiltonian minus the post-quench ground state eigenvalue, per lattice site (in units \( J = 1 \)). One can put a simple upper bound on the particle density by dividing the energy density with the value of the gap. For the critical value \( h_x = 0.04 \) at \( h_x = 1.25 \) the upper bound on the particle density is about one particle per 70 lattice sites, while for the critical value \( h_x = 0.14 \) at \( h_x = 1.5 \) this results in a density of about one particle per 35 lattice sites. Even for the case \( h_x = 0.4 \) at \( h_x = 2 \) the upper bound is one particle per 25 lattice sites, still a very low density compared to the correlation length \( \xi \) which can be bounded from above.

| \( h_x \) | 0.18 | 0.25 | 0.30 |
|-----------|------|------|------|
| \( v_{\text{max}}^{(2)} \) | 1.579 | 1.413 | 1.295 |

Table \( IV \). Values of the Lieb-Robinson velocity determined from the data shown in Fig. \( [6] \) decreases as shown in Table \( [IV] \).
Figure 4. Gap ratio $\Delta_{21}$ defined in (10) as a function of $h_x$.

Figure 5. Interaction strength $\gamma_{21}$ defined in (10) as a function of $h_x$.

by its value at $h_x = 0$ \[ \xi = \frac{1}{\log|h_z|} = \begin{cases} \frac{4.48}{\log(1.25)} & h_z = 1.25 \\ \frac{2.47}{\log(1.5)} & h_z = 1.5 \\ \frac{1.44}{\log(2.0)} & h_z = 2.0 \end{cases} \] given in number of lattice sites. This demonstrates that the post-quench particle density is very small for the parameter range of interest.

IV. RELATION TO THE GIBBS PARADOX

In the following table the positions $h_{x}^{\text{min}}$ of the minima of the mean entropy production rate $\frac{\partial}{\partial t}S$ (Table I) are compared with the threshold values $h_{x}^{(2)}$ where the second bound state appears (Table III)

| $h_z$  | 1.25 | 1.5 | 1.75 | 2   |
|-------|------|-----|------|-----|
| $h_{x}^{\text{min}}$ | 0.040 | 0.140 | 0.268 | 0.412 |
| $h_{x}^{(2)}$ | 0.040 | 0.146 | 0.261 | 0.400 |

A crucial observation is that these values are very close:
for smaller values of $h_z$ they eventually coincide within numerical accuracy, while for the higher values $h_z = 1.75$ and $h_z = 2$ the minimum appears at a slightly larger $h_x$ than the bound state threshold.

For the interpretation of these results it is important to recall first that at late times the asymptotic entanglement entropy of a large subsystem can be interpreted as the thermodynamic entropy $S$ [12, 33, 37, 51]. To understand the association between the bound states and the entropy production rate, we turn to a quasi-particle description of entropy production. The quasi-classical picture of quench dynamics [10] describes the initial state as a source of entangled quasi-particle pairs which propagate to different parts of the system, resulting in the build-up of spatial correlations and entanglement growth. This picture was explicitly demonstrated for integrable quenches in the Ising spin chain [49] and also forms the basis of a semi-classical approach for quantum quenches [50], which is expected to be valid for sufficiently small post-quench density even in the non-integrable case. It also successfully describes entropy production in integrable systems [33, 35, 51] and leads to the following formula for the late time growth of the entanglement entropy of a subsystem of size $\ell$ [12, 33, 35]:

$$S(t) \propto 2t \sum_n \int_{2v_n t < \ell} dk v_n(k) f_n(k) + \ell \sum_n \int_{2v_n t > \ell} dk f_n(k),$$

(13)

where $n$ enumerates the different quasi-particle species, $k$ is the momentum of the quasi-particles, $v_n(k)$ is their velocity and $f_n(k)$ is a rate function describing the entropy produced by quasi-particle pairs of species $n$ which depends on their production rate. For the half-system ($\ell = \infty$) entanglement entropy the second term describing saturation is absent, and the integral in the first one has no restriction, so it simplifies to

$$S(t) \propto 2t \sum_n \int dk v_n(k) f_n(k).$$

(14)

Eq. (13) suggests that the entanglement production rate is a slowly varying function of the quench parameter $h_x$ and the data in Fig. 1 show that this is indeed true below the threshold $h_x^{(2)}$. Note that after an initial rise, the contribution from the first species $(A_1)$ decreases which is explained below in terms of the quasi-particle spectrum. If the effect of the new quasi-particle $(A_2)$ simply added the contribution of pairs $A_2 A_2$, it should have the same behavior as the contribution from pairs $A_1 A_1$, except being smaller due to the even larger gap and smaller quasi-particle velocity.

However, as demonstrated in Fig. 1 the entanglement production rate increases by an order of magnitude after passing the threshold, an effect which is really pronounced even closer to the critical point $h_z = 1$. The flaw in

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2 The restriction in the integral leads to light-cone propagation as a consequence of the Lieb–Robinson bound.

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Figure 6. The second quasi-particle dispersion relation for $h_x = 1.5$ and $h_x = 0.18, 0.25$ and 0.30. The differently colored dots are energy levels computed for systems sizes of $L = 16, 18, 20$ and 22 spins, illustrating that finite size dependence is already negligible. The continuous lines are fits of a function $\epsilon_2(k) = \sqrt{A + B \cos k + C \cos 2k}$.

Figure 7. The energy density after a quantum quench from $h_z = 0$ to $h_z \neq 0$ for $h_x = 1.25$ and 1.5.
the naive argument is that it neglects the contribution of species mixing, which is the cornerstone of the classical Gibbs paradox. In the usual setting of the paradox one takes a box divided by a wall into two equal halves, with \( N \) particles in each. Even though removing the wall is reversible by reinserting it, a simple computation using ideal gas laws shows that it increases the thermodynamic entropy by an amount \( \Delta S = 2k_B \ln 2 \). The key to resolving the paradox is to specify the relation between particles in the two halves: for indistinguishable particles, this term is not present, while if the particles are distinguishable, it corresponds to their mixing entropy and removing the wall is indeed an irreversible process.

Similarly, the appearance of the second quasi-particle increases the thermodynamic entropy produced in the quench by the species information. This is supported by the finding that in the continuum limit of the Ising spin chain, quenching in \( h_x \) results in the creation of mixed pairs \( A_1, A_2 \) \cite{[52]}. The presence of mixed pairs means that the entropy carried by the quasi-particles contains species information, i.e. the Gibbs mixing entropy. In Appendix \( \Delta \) we demonstrate via a semiclassical estimate using features of the pair amplitudes from the field theory and a construction recently developed in \cite{[51]}, that the mixed pairs indeed lead to an increase of roughly the observed magnitude in the entropy production rate.

It is important to realize that in spite of the non-integrability of the system, the quasi-particle picture is still expected to be a good approximation. The reason is that turning on a longitudinal field in the paramagnetic regime does not lead to a drastic change in the physical behavior contrary to the ferromagnetic case \cite{[50]}, where it triggers confinement \cite{[53]}. Fig. 8 presents power spectra obtained from

\[
\sigma^\alpha(t) = \int_0^\infty dt e^{i\omega t} \langle \sigma^\alpha(t) \rangle,
\]

where \( \langle \sigma^\alpha(t) \rangle \) (\( \alpha = x, z \)) are the longitudinal and transverse magnetizations. These show clear quasi-particle peaks at the frequencies predicted by the exact diagonalization results in Section \( \text{III} \). In addition, the self-consistency of the quasi-particle description is also demonstrated by the small values of the upper limits of the post-quench particle density obtained in Subsection \( \text{III.D} \).

To explain the decrease of the entropy production rate below \( h_x^{(2)} \) seen in Fig. 1, note that both the exact diagonalization results (Fig. 3) and the power spectra (Fig. 8) show that the particle masses (excitation gaps) increase with \( h_x \). Even though the post-quench energy density \( \langle \Psi_0|H|\Psi_0 \rangle - E_0 \)/\( L \) increases with \( h_x \), its ratio with the energy gap saturates, which is also consistent with the stagnation of the size of the quasi-particle peaks in Fig. 8. This gives a (very rough) upper bound on the particle density in the initial state, and so the rate functions \( f_n(k) \) (while not directly accessible) are also expected to stop growing with \( h_x \). Moreover, only a small fraction of the quasi-particle excitations propagates at the maximum velocity; this fact, joined with the global decrease (for all momenta) of the quasi-particle velocities \( v_n(k) \) with \( h_x \) explains why the late time mean entropy production rate \( \overline{\partial_t S} = 2 \sum_n \int dk v_n(k) f_n(k) \) decreases for \( h_x < h_x^{(2)} \).

Albeit the trend change in \( \overline{\partial_t S} \) as a function of \( h_x \) is rapid, it is not a discontinuous jump due to several reasons. First, the heavier second excitation is produced with a density that smoothly depends on the quench parameter \( h_x \) and increases only gradually. Second, the distinguishability of the second quasi-particle peak also increases gradually with \( h_x \). As shown by the power spectra in Fig. 8 at first the second quasi-particle peak is not prominent and is barely distinguishable from the continuum background. As known in the case of the equilibrium Gibbs paradox \cite{[54, 55]}, distinguishability is a key feature governing the effective number of species contributing to thermodynamic quantities such as free energy and entropy. Third, the post-quench system is filled with a finite density “plasma” of excitations which leads to a finite life-time of the quasi-particle excitations, and is also known to lead a shift in the effective quasi-particle masses \cite{[56]}. In case of very weakly bound quasi-particles (such as the third quasi-particle which does exist at zero temperature/density for suitably large \( h_x \)), the plasma effect can even suppress the signal completely by destabilizing the excitations. This effect is completely consistent with, and indeed explains, the observation that the difference between \( h_x^{(2)} \) and \( h_x^{\text{min}} \) grows with increasing \( h_x \).

As a consequence of the gradual change of the effective number of quasi-particle species characterizing the post-quench state, the simple summation over quasi-particle species appearing in Eq. (13) does not eventually apply in the region around the threshold. Therefore a quantitative explanation of \( \overline{\partial_t S} \) as a function of \( h_x \) requires a more complete theory of entropy production with multiple quasi-particle species after a non-integrable quench, which at this point is left open for the future. While this affects the exact definition of the rate functions \( f_n(k) \), it is not expected to alter the relation between the asymptotic entropy density and entanglement production rate (the two terms of Eq. 13) which is a general consequence of the quasi-particle picture alone.

V. DISCUSSION

In this paper we found an anomalous increase of the entropy production rate due to the appearance of bound states in the quantum Ising spin chain quenched by switching on a longitudinal magnetic field at a fixed value of the transverse field in the paramagnetic phase. The anomaly is clearly related to the appearance of a new quasi-particle state in the spectrum, and its details confirm that the effect is a dynamical manifestation of the Gibbs paradox well-known from equilibrium statistical mechanics. We remark that after the completion of this work, new results obtained for the 3-state Potts spin
Figure 8. Fourier transforms of the time dependence of longitudinal ($\alpha = x$) and transverse ($\alpha = z$) magnetizations. For each $h_z$ the three plots shown are before/around/beyond the critical value $h_{z}^{\text{crit}}$. The (blue/purple) vertical dash-dotted lines are the expected positions of the peaks corresponding to the first and second quasi-particles $A_1$ and $A_2$. For the bottom plots which are below threshold, the second vertical line corresponds to the energy of the lowest lying two-particle state, which turns into a zero-momentum $A_2$ state for $h > h_x^{(2)}$. Note that for large enough $h_z$ a third peak emerges in the spectrum, which is the precursor of the third quasi-particle $A_3$ discussed in Subsection IIIC.

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Appendix A: A semiclassical calculation

To illustrate the mechanism behind the increase of entanglement growth, in this appendix we present a semiclassical calculation in systems with two distinguishable species of free fermions. We follow and extend the method introduced in the recent work [68]. On the one hand, the fermionic algebra considerably simplifies the calculation, on the other hand it serves as a first approximation to the system studied in this paper insofar as the lightest particle is a genuine free fermion for $h_x = 0$.

We assume that during the quench entangled pairs of quasi-particles are created with opposite momenta. The initial state (in a finite volume) thus can be written as

$$|\Psi_0\rangle = N \prod_{k>0} \left[ 1 + A(k)a_k^{\dagger}a_{-k}^{\dagger} + B(k)b_k^{\dagger}b_{-k}^{\dagger} + C(k)a_k^{\dagger}b_{-k}^{\dagger} + D(k)b_k^{\dagger}a_{-k}^{\dagger} \right] |0\rangle,$$  \hspace{1cm} (A1)

where $|0\rangle$ is the post-quench ground state, $N$ is a normalization factor, and $a_k^{\dagger}$ and $b_k^{\dagger}$ are the annihilation (creation) operators of the first and the second particle, respectively, obeying anticommutation relations

$$\{a_p, a_q^{\dagger}\} = \{b_p, b_q^{\dagger}\} = \delta_{p,q}, \quad \{a_p, b_q\} = \{a_p^{\dagger}, b_q^{\dagger}\} = 0.$$  \hspace{1cm} (A2)

The product in Eq. (A1) runs over positive momenta quantized in a finite volume $L$. Note that we allow for the creation of mixed pairs consisting of an $a$-type and a $b$-type particle. Using the fermionic algebra one can compute the normalization factor with the result

$$N = \prod_{k>0} N_k = \prod_{k>0} \left( 1 + |A(k)|^2 + |B(k)|^2 + |C(k)|^2 + |D(k)|^2 \right)^{-1/2}.$$  \hspace{1cm} (A3)

The density matrix also factorizes into momentum sectors,

$$\hat{\rho}_0 = |\Psi_0\rangle \langle \Psi_0| = \prod_{k>0} \hat{\rho}_{k,-k}.$$  \hspace{1cm} (A4)

The idea behind the semiclassical picture for entanglement generation is that a spatial subsystem becomes
entangled with the rest of the system via the entanglement of particle pairs for which one member of the pair is inside the subsystem while the other member is outside of it \[59\]. Each momentum sector thus contributes by the entanglement entropy between the two modes of momentum \(k\) and \(-k\), so we need to compute the reduced density matrices

\[
\hat{\rho}_k = \mathcal{N}_k^2 \left[ \langle 0 | 0 \rangle + (|A(k)|^2 + |C(k)|^2) a_k^\dagger |0\rangle \langle 0 | a_k + (|B(k)|^2 + |D(k)|^2) b_k^\dagger |0\rangle \langle 0 | b_k \\
+ [A(k) D(k)^* + B(k)^* C(k)] a_k^\dagger |0\rangle \langle 0 | b_k + [A(k)^* D(k) + B(k) C(k)^*] b_k^\dagger |0\rangle \langle 0 | a_k \right],
\]

where we dropped the \(-k\) subscript from the Fock vacuum state \(|0\rangle\). The corresponding entanglement entropy is then

\[
S_k = -\text{Tr}_\rho \hat{\rho}_k \log \hat{\rho}_k .
\]

At time \(t\) only those pairs contribute to the half space entanglement entropy that come from the \([-v_k t, v_k t]\) interval, which in the infinite volume limit leads to

\[
S(t) = -\int \frac{dk}{2\pi} 2v_k t \text{Tr}_\rho \hat{\rho}_k \log \hat{\rho}_k ,
\]

an entanglement entropy growing linearly in time.

Let us analyze how the contribution \(S_k\) of the \(\{k, -k\}\) sector is affected by the presence of mixed pairs. \(S_k\) depends on the four amplitudes which we fix using the numerical values that were measured in Ref. \[60\] for a similar quench in the continuum Ising field theory (see Fig. 5.4 there). In particular, we set \(A(k) = 0.005, C(k) = D(k)\) due to parity symmetry, and a relation between \(B(k)\) and the mixing amplitudes: \(C(k) = D(k) = 1.6 B(k)\). Keeping \(A(k)\) fixed is a meaningful choice because we are interested in the change of the entanglement production rate around the threshold for the second particle, where \(B(k)\) starts to grow from zero but \(A(k)\) is approximately constant.

In the left panel of Fig. 9 we plot \(S_k\) both in the presence (solid curve) and in the absence \((C(k) = D(k) = 0)\) of mixed pairs (dashed curve) in the initial state as a function of the creation amplitude \(B(k)\) of the second particle. It is clear that in accordance with the Gibbs mixing entropy, the presence of mixed pairs leads to an enhancement of the entanglement entropy and of the entanglement generation rate. In the right panel the ratio of the two curves are plotted demonstrating that passing the threshold there is a sudden and significant increase in the entanglement entropy as a result of the mixed pairs.
Appendix B: Numerical simulation of time evolution

Numerical simulations of the quench dynamics in the non-integrable Ising chain was performed using the infinite volume Time-Evolving Block-Decimation (iTEBD) algorithm [39]. The algorithm exploits the translational invariance of the system by representing a generic many-body state on a one-dimensional lattice as

$$|\Psi\rangle = \sum_{\cdots s_j, s_{j+1}, \cdots} \cdots \Lambda_o \Gamma_o^s \Lambda_e \Gamma_e^{s_{j+1}} \cdots |\cdots, s_j, s_{j+1}, \cdots\rangle,$$

(B1)

where $s_j$ spans the local spin-1/2 Hilbert space, $\Gamma_o/e$ are $\chi \times \chi$ matrices associated with the odd/even lattice site; $\Lambda_o/e$ are diagonal $\chi \times \chi$ matrices with the singular values corresponding to the bipartition of the system at the odd/even bond as their entries. The many-body state is initialized to the product state $|\Psi_0\rangle = \bigotimes (|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}$.

The Matrix Product State (MPS) representation of the ground state $|\Psi_{GS}\rangle$ is obtained by time-evolving the initial state $|\Psi_0\rangle$ in imaginary time. We used a second-order Suzuki-Trotter decomposition of the evolution operator with imaginary time Trotter step $\tau = 10^{-4}$. The Hamiltonian was been tuned to the paramagnetic phase of the model, namely $h_z = 0$ and $h_z \in \{1.25, 1.5, 1.75, 2\}$. Due to the presence of an energy gap separating the ground state from the rest of the spectrum, an auxiliary dimension $\chi_0 = 32$ was sufficient to have a very accurate MPS description of the ground state.

Similarly, the post-quench time evolution was obtained by evolving the corresponding ground state with a new Hamiltonian with $h_x \neq 0$ in real time. For this purpose again a second-order Suzuki-Trotter decomposition of the evolution operator was used, with real time Trotter step $dt = 10^{-3}$. In order to keep the truncation error as small as possible, the auxiliary dimension was allowed to grow up to $\chi_{MAX} = 512$ which was sufficient to reach a maximum time $T = 60$. The ability to reach relatively large times is related to the dynamical properties of the system under investigation. As explained in the main text, for such class of quenches, the bipartite entanglement entropy does not grow significantly as long as $h_x$ is “sufficiently” small. For $h_x$ larger than the critical threshold, the bipartite entanglement entropy starts growing faster, nonetheless always remaining smaller than $\simeq 3$. After a relatively short transient, the numerical data for the entanglement entropy showed a linear increase (apart from oscillations) whose slope depends on the particular value of the longitudinal field exactly as expected after a global quantum quench. In particular, a numerical estimation of the entanglement entropy slope $\partial_t S$ has been obtained by performing a linear fit of the iTEBD data in the time-window $30 \leq t \leq 60$ (cf. Fig. 1).

Similarly, the iTEBD simulation allows us to trace the expectation value of local observables easily. In particular, we analyzed the longitudinal $\langle \sigma^z(t) \rangle$ and transverse $\langle \sigma^x(t) \rangle$ magnetizations. From the corresponding time series, the power spectra $\sigma^z/\omega$ were obtained using FFT (see Fig. 5), with an angular frequency resolution $d\omega = 2\pi/T \simeq 0.10472$. The second peak in the power spectrum which appears above the critical value of $h_x$ is the signature of a new bound state, in agreement with the predicted spectrum from exact diagonalization.