Universal Energy Fluctuations in Inelastic Scattering Processes

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Quantum scattering is used ubiquitously in both experimental and theoretical physics across a wide range of disciplines, from high-energy physics to mesoscopic physics. In this Letter, we uncover universal relations for the energy fluctuations of a quantum system scattering inelastically with a particle at arbitrary kinetic energies. In particular, we prove a fluctuation relation describing an asymmetry between energy absorbing and releasing processes which relies on the nonunital nature of the underlying quantum map. This allows us to derive a bound on the average energy exchanged. We find that energy releasing processes are dominant when the kinetic energy of the particle is comparable to the system energies, but are forbidden at very high kinetic energies where well-known fluctuation relations are recovered. Our Letter provides a unified view of energy fluctuations when the source driving the system is not macroscopic but rather an auxiliary quantum particle in a scattering process.

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Introduction—Scattering is a mechanism of interaction between physical systems that is pervasive across nature and experiment, from low to high energies [1,2]. It is an essential tool in the characterization of materials and quantum phenomena in condensed matter [3,4], in describing the transport properties of quantum systems [5–10] and the properties of ultracold gases [11–19]. Quantum scattering theory describes how two (or more) quantum systems change their state after they collide, which entails an energy exchange between them when the scattering process is inelastic [1–3]. Such energy exchanges have been recently analyzed from a thermodynamic viewpoint, showing that a particle colliding with a quantum system can act as a source of heat [20–22] or work [23]. Very massive particles can also be used to probe the energy statistics that would result from a two-point measurement scheme on the system [24]. Although these studies validate scattering as a powerful microscopic approach to thermodynamics of quantum systems, a more general treatment at the level of energy fluctuations is still not available.

In thermodynamics, energy fluctuations are usually studied for small—classical or quantum—systems interacting with macroscopic sources. The assumption of a macroscopic source allows us to define some Hamiltonian for the system with a time-dependent parameter that we imagine is operated in a classical way [25]. Within this paradigm, some of the most famous results of stochastic thermodynamics have been derived, for example, the so-called fluctuation relations [26–31]. As an example, consider a system of any size prepared in thermal equilibrium with its environment characterized by $\beta = 1/k_B T$, where k_B is the Boltzmann constant and T is the temperature. When the system is driven out of equilibrium by a macroscopic source in a cyclic fashion (so that the system Hamiltonian is the same before and after the interaction), then the fluctuation relation reads $e^{-\beta W} p_W = \tilde{p}_{-W}$, where p_W is the probability distribution for an energy change W during the process and $\tilde{p}_{-W}$ is the probability distribution for an energy change $-W$ in the time-reversed process [29,30]. Jarzynski's equality $\langle e^{-\beta W} \rangle = 1$ [32] follows by a simple average over W which, through Jensen's inequality, implies (on average) the impossibility of energy extraction in a cyclic process $\langle W \rangle \geq 0$. Since the macroscopic source is considered to behave deterministically, i.e., as a work source, the energy consumed is interpreted as work done on the system. Through the use of the two-point measurement scheme, fluctuation relations have been extended to closed quantum systems [33–38], derived for macroscopic heat sources [29,39], and experimentally verified across different platforms [40–44].

A valid framework to go beyond the macroscopic source paradigm is that of open quantum systems [45,46], where the system dynamics is described by a dynamical map [47–50] obtained after the interaction with

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another quantum system of arbitrary size. It is known that fluctuation relations can be derived within the two-point measurement scheme when the map is unital, i.e., if the maximally mixed state is an invariant state [41,51,52]. If the map is not unital, it has been shown that Jarzynski's equality is modified to $\langle e^{-\beta W}\rangle = 1+\eta$, where η can be positive or negative [52–55]. This generalized equality has been experimentally verified with entangled photons subject to turbulence [56] and also appears in studies of fluctuations with generalized measurements [57] and feedback control [58,59]. Since Jensen's inequality then implies $\langle W\rangle \geq -\beta^{-1}\log(1+\eta)$, this suggests that $\eta > 0$ allows for energy releasing processes; indeed, such processes are necessary for cooling quantum systems [38]. Despite their clear relevance for thermodynamics, the physics behind nonunital fluctuations remains poorly understood and appreciated. Arguably, this is due to the fact that previous studies [52–55] focus on the properties of the dynamical map rather than on a quantum mechanical description of the interacting systems. Progress could be made by using a realistic and microscopic approach like quantum scattering theory, whereby one treats the interacting systems as quantum systems in their own right, potentially providing a unified view of energy fluctuations beyond the macroscopic source limit.

In this Letter, we provide such a unified view on energy fluctuations by studying a quantum system scattering inelastically with a particle at an arbitrary kinetic energy. The dynamical map for the system naturally encodes its energy fluctuations without relying on any measurement scheme. Our main result [Eq. (8)] describes a universal fluctuation relation obeyed for a system driven out of equilibrium by the colliding particle and reflects the nonunital nature of the scattering process. From this result, we derive an exact bound for the energy exchanged [Eqs. (10) and (11)] as a function of the particle's kinetic energy. We show that nonunitality dominates when the particle's kinetic energy is comparable to the energy gaps of the system, allowing energy extraction from the system, while at very high kinetic energies we recover unitality and the standard fluctuation relation. Our results show that nonunital fluctuation relations are intimately connected with the energy of the quantum source, which can be of the same order as energy fluctuations themselves.

Setup and energy fluctuations—We consider a quantum scattering process between a system S and a particle P. In a reference frame comoving with the center of mass, only the reduced mass plays a role, but we simplify the treatment by fixing the position of system S and consider the particle P to be traveling in one direction with associated momentum $\hat{p}$ and position $\hat{x}$ operators. The total Hamiltonian is $\hat{H} = \hat{H}_0 + \hat{V}(\hat{x})$, where $\hat{H}_0 = \hat{H}_S \otimes \hat{\mathbb{I}}_P + \hat{\mathbb{I}}_S \otimes \hat{p}^2/2m$ is the bare Hamiltonian. The energy of the system is defined by $\hat{H}_S|j\rangle = e_j|j\rangle$, where $\{|j\rangle\}$ is a basis of eigenvectors associated to its discrete energy spectrum $\{e_j\}$. The energy of the particle is described by $\hat{p}^2/2m|p\rangle = E_p|p\rangle$, where $\{|p\rangle\}$ are improper (non-normalizable) eigenvectors whose position representation are plane waves $\langle x|p\rangle = \exp(ipx/\hbar)/\sqrt{2\pi\hbar}$ and $E_p = p^2/2m \geq 0$ is the kinetic energy. The interaction operator $\hat{V}(\hat{x})$ is assumed to vanish sufficiently far away from the scattering region where the system is located, so that the unitary scattering operator $\hat{S} = \lim_{t\to+\infty} e^{(it/\hbar)\hat{H}_0} e^{-(i2t/\hbar)\hat{H}} e^{(it/\hbar)\hat{H}_0}$ exists and satisfies energy conservation $[\hat{S}, \hat{H}_0] = 0$ [1,2]. Considering the initial state of the system $\hat{\rho}_S$ and particle $\hat{\rho}_P$ to be uncorrelated before the collision, the state of the system after the collision is

$$\Phi(\hat{\rho}_S) = \mathrm{Tr}_P[\hat{S}(\hat{\rho}_S \otimes \hat{\rho}_P)\hat{S}^\dagger], \tag{1}$$

where Tr_P is the partial trace over the particle and Φ is a completely positive and trace preserving map [45–48,50].

The explicit evaluation of Eq. (1) can be performed in the following kinetic energy eigenstates, $|E_p^\alpha\rangle \equiv \sqrt{m/|p|}|p\rangle$, where $\alpha = \mathrm{sgn}(p)$ accounts for the initial direction of the incoming particle, which can be traveling to the left ($\alpha = +$) or right ($\alpha = -$). First, we need the representation of the scattering operator in this basis which reads $\langle E_{p'}^{\alpha'}|\hat{S}|E_p^\alpha\rangle = \sum_{j',j}|j'\rangle\langle j|\langle E_{p'}^{\alpha'}, j'|\hat{S}|E_p^\alpha, j\rangle$, where $|E_p^\alpha, j\rangle$ is the eigenbasis of $\hat{H}_0$ and $\langle E_{p'}^{\alpha'}, j'|\hat{S}|E_p^\alpha, j\rangle = \delta(E_{p'} + e_{j'} - E_p - e_j)s_{j'j}^{\alpha'\alpha}(E_p + e_j)$. In the last expression, the δ function ensures energy conservation for the collision and $s_{j'j}^{\alpha'\alpha}(E)$ is the scattering matrix encoding the transition amplitudes from $|E_p^\alpha, j\rangle \to |E_{p'}^{\alpha'}, j'\rangle$ at total energy $E = E_p + e_j$ [1,2]. Rewriting the sum over j', j as a sum over energy differences Δ then yields simply $\langle E_{p'}^{\alpha'}|\hat{S}|E_p^\alpha\rangle = \sum_\Delta \delta(E_{p'} - E_p + \Delta)\hat{S}_\Delta^{\alpha'\alpha}(E_p)$, where

$$\hat{S}_\Delta^{\alpha'\alpha}(E_p) = \sum_{\substack{j',j:\\ e_{j'}-e_j=\Delta}} s_{j'j}^{\alpha'\alpha}(E_p + e_j)|j'\rangle\langle j| \tag{2}$$

are eigenoperators of $\hat{H}_S$ and thus obey $[\hat{H}_S, \hat{S}_\Delta^{\alpha'\alpha}(E_p)] = \Delta\hat{S}_\Delta^{\alpha'\alpha}(E_p)$. Second, we need the representation of the particle's state in the same basis $\rho_P^{\alpha\beta}(E_p, E_q) \equiv \langle E_p^\alpha|\hat{\rho}_P|E_q^\beta\rangle$ and we can carry out the trace in Eq. (1). After integrating the δ functions, we find that the particle's state becomes dependent on the energy differences as $\rho_P^{\alpha\beta}(E_p, E_p - \Delta + \Delta')$ [60]. However, as shown in Ref. [20], if the particle has a well-defined direction before the collision and is sufficiently narrow in kinetic energy with respect to the energy differences, then we can write

$$\rho_P^{\alpha\beta}(E_p, E_p - \Delta + \Delta') \simeq \delta_{\alpha\beta}\delta_{\Delta\Delta'}\rho_P^\alpha(E_p), \tag{3}$$

where $\rho_P^\alpha(E_p) \equiv \rho_P^{\alpha\alpha}(E_p, E_p)$ is the kinetic energy distribution for a particle traveling with direction α. In this case, Eq. (1) can be written as

$$\Phi(\hat{\rho}_S) = \int dE_p \sum_{\alpha=\pm} \rho_P^\alpha(E_p)\Phi^\alpha(E_p)(\hat{\rho}_S), \tag{4}$$

where $\Phi^\alpha(E_p)$ is a completely positive and trace preserving map conditioned on the particle's kinetic energy E_p and direction α given by

$$\Phi^\alpha(E_p)(\cdot) = \int dW \Phi^\alpha(E_p, W)(\cdot), \tag{5}$$

$$\Phi^\alpha(E_p, W)(\cdot) = \sum_\Delta \delta(W-\Delta) \sum_{\alpha'} \hat{S}_\Delta^{\alpha'\alpha}(E_p)\cdot \hat{S}_\Delta^{\alpha'\alpha}(E_p)^\dagger. \tag{6}$$

Equations (4)–(6) define the dynamical map (see Fig. 1).

Note that the Kraus operators in Eq. (6) are system eigenoperators due to condition (3), inducing a transition with energy change Δ. Indeed, assuming that $\hat{H}_S$ has a nondegenerate spectrum, it is easy to see that the quantum operation in Eq. (6) defines a probability distribution for the energy changes through

$$\begin{aligned} P^\alpha(E_p, W) &= \mathrm{Tr}_S[\Phi^\alpha(E_p, W)(\hat{\rho}_S)] \\ &= \sum_{j',j} \delta(W - e_{j'} + e_j) P^\alpha_{j'j}(E_p + e_j) p_j, \end{aligned} \tag{7}$$

where $p_j \equiv \langle j|\hat{\rho}_S|j\rangle$ and $P^\alpha_{j'j}(E_p + e_j) = \sum_{\alpha'} |s^{\alpha'\alpha}_{j'j}(E_p + e_j)|^2$ is the transition probability. Note that Eq. (7) has the same form as the distribution for energy changes induced by a unitary operator U on the system in a two-point measurement scheme [29,30,33,34,36], with two crucial differences. First, there is no need for a two-point measurement scheme as a consequence of condition (3): a particle with a well-defined kinetic energy effectively measures the energy changes in the system [24]. Second, the transition probabilities are dictated by $P^\alpha_{j'j}(E_p + e_j)$ instead of $|\langle|j'|U|j\rangle|^2$, thus becoming dependent on both the system and the particle's energy. The normalization $\int P^\alpha(E_p, W)dW = \sum_{j',j} P^\alpha_{j'j}(E_p + e_j)p_j = 1$ holds since the map in Eq. (5) is trace preserving by construction. Indeed, the property $\sum_{j'} P^\alpha_{j'j}(E_p + e_j) = 1$ can be proven independently from the unitarity of the scattering operator and holds for any fixed total energy E [20,60].

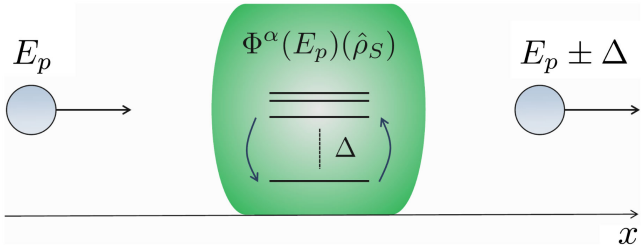

FIG. 1. A particle with kinetic energy E_p travels in space with direction α and scatters with the system initially in state $\hat{\rho}_S$. The map $\Phi^\alpha(E_p)$ encodes the evolution and energy fluctuations of the system as defined in Eqs. (5) and (6). The direction of the particle is to the left $\alpha = +$ in this schematic for illustrative purposes.

Main result—We now take our system to be in a thermal state $\hat{\rho}_S = e^{-\beta\hat{H}_S}/Z$, where $Z = \mathrm{Tr}_S[e^{-\beta\hat{H}_S}]$ is the partition function [61]. Using the property of the eigenoperators $\hat{S}_\Delta^{\alpha'\alpha}(E_p)e^{-\beta\hat{H}_S} = e^{\beta\Delta}e^{-\beta\hat{H}_S}\hat{S}_\Delta^{\alpha'\alpha}(E_p)$, it is easy to see that the quantum operation satisfies $e^{-\beta W}\Phi^\alpha(E_p, W)(\hat{\rho}_S) = \hat{\rho}_S\Phi^\alpha(E_p, W)(\hat{\mathbb{I}}_S)$, and thus the distribution in Eq. (7) obeys

$$e^{-\beta W}P^\alpha(E_p, W) = \mathbb{P}^\alpha(E_p, -W), \tag{8}$$

where $\mathbb{P}^\alpha(E_p, -W)$ is dual probability distribution given by

$$\begin{aligned} \mathbb{P}^\alpha(E_p, -W) &= \mathrm{Tr}_S[\Phi^\alpha(E_p, W)^\dagger(\hat{\rho}_S)] \\ &= \sum_{j',j} \delta(-W - e_j + e_{j'}) p_{j'} P^\alpha_{j'j}(E_p + e_j), \end{aligned} \tag{9}$$

with the dual operation defined by $\mathrm{Tr}_S[\hat{\rho}_S\Phi^\alpha(E_p, W)(\hat{\mathbb{I}}_S)] = \mathrm{Tr}_S[\Phi^\alpha(E_p, W)^\dagger(\hat{\rho}_S)]$. Equation (9) has the same form as the distribution for energy changes induced by a time-reversed unitary operator $U^\dagger = \Theta U \Theta^\dagger$ on the system in a two-point measurement scheme, where Θ is the (antiunitary) time-reversal operator [29,30,33,34,36]. In this sense, the dual operation $\Phi^\alpha(E_p, W)^\dagger$ reverses the energy change induced by $\Phi^\alpha(E_p, W)$ [62]. However, a crucial point is that the dual distribution in Eq. (9) is generally not normalized, $\gamma^\alpha(E_p) \equiv \int \mathbb{P}^\alpha(E_p, -W)dW = \sum_{j',j} p_{j'} P^\alpha_{j'j}(E_p + e_j) \neq 1$. This reflects the fact that the map in Eq. (5) is nonunital, or equivalently that its dual is not trace preserving [51–53,55]; unitality would require $\sum_j P^\alpha_{j'j}(E_p + e_j) = 1$ which is generally not obeyed in quantum scattering theory. Below, we show that both nonunitality and unitality are general features of the scattering process and discuss the physical conditions where each arises.

From our main result in Eq. (8) we can obtain an integral fluctuation relation $\int e^{-\beta W}P^\alpha(E_p, W)dW = \gamma^\alpha(E_p)$. Using the fact that $[\hat{H}_S, \Phi^\alpha(E_p)(\hat{\mathbb{I}}_S)] = 0$ (which follows from the properties of the eigenoperators [60]), we can recast the normalization of the dual distribution as $\gamma^\alpha(E_p) = \int \mathbb{P}^\alpha(E_p, -W)dW = Z^{-1}\mathrm{Tr}_S[e^{-\beta\hat{H}_S}\Phi^\alpha(E_p)(\hat{\mathbb{I}}_S)] = Z^\alpha(E_p)/Z$, where $Z^\alpha(E_p) = \mathrm{Tr}[e^{-\beta\hat{H}^\alpha_S(E_p)}]$ is the partition function associated with a new system Hamiltonian $\hat{H}^\alpha_S(E_p) \equiv \hat{H}_S - \beta^{-1}\log\Phi^\alpha(E_p)(\hat{\mathbb{I}}_S)$ which depends on the dynamical map itself. The integral fluctuation relation then reads $\int e^{-\beta W}P^\alpha(E_p, W)dW = e^{-\beta\Delta F^\alpha(E_p)}$, where $\Delta F^\alpha(E_p) = -\beta^{-1}\log[Z^\alpha(E_p)/Z]$ with $Z^\alpha(E_p)/Z = \gamma^\alpha(E_p)$ describes

the free energy available from the nonunitality of the process; by its definition, it evidently vanishes for unital maps. Through Jensen's inequality, we obtain the following lower bound for the average energy change,

$$\langle W\rangle^{\alpha}(E_p) \geq \Delta F^{\alpha}(E_p), \tag{10}$$

where $\langle W\rangle^{\alpha}(E_p) \equiv \int W P^{\alpha}(E_p, W) dW$. The sign of the lower bound is determined by the sign of the quantity $\eta^{\alpha}(E_p) \equiv \gamma^{\alpha}(E_p) - 1$. When $\eta^{\alpha}(E_p) > 0$ the lower bound in Eq. (10) becomes negative and an initially thermal system can release energy in the collision, while when $\eta^{\alpha}(E_p) \leq 0$ it is impossible to extract energy from the system, with the equality holding for unital dynamics. It can be shown that $\eta^{\alpha}(E_p)$ has the exact form [60]

$$\eta^{\alpha}(E_p) = \sum_{\Delta>0} \tanh\left(\frac{\beta\Delta}{2}\right) \sum_{\substack{j',j:\\ e_{j'}-e_j=\Delta}} \left(\frac{Z_{j'j}}{Z}\right) \times [P^{\alpha}_{jj'}(E_p + e_{j'}) - P^{\alpha}_{j'j}(E_p + e_j)]. \tag{11}$$

The first sum in the last expression is over all the energy gaps of the system. For a given energy gap $\Delta > 0$, the second sum is over all pairs of energy levels whose difference is Δ, and $Z_{j'j} = e^{-\beta e_{j'}} + e^{-\beta e_j}$ is the partition function of one of these pairs. The last term describes the imbalance between relaxation and excitation probabilities of the pair, being positive (negative) when the former are higher (lower) than the latter.

Discussion and example—In general, it is difficult to predict the behavior of $\langle W\rangle^{\alpha}(E_p)$ and $\eta^{\alpha}(E_p)$, since they depend strongly on the scattering matrix, which in turn depends on the system Hamiltonian $\hat{H}_S$ and scattering potential $\hat{V}(\hat{x})$. Whenever there is access to the multichannel scattering matrix (or collision cross section), such as in ultracold atom experiments (see, e.g., Refs. [14,15]), these quantities can be determined. However, we can study their behavior more generally based on universal scattering features in two regimes: when the kinetic energy is comparable to the minimum energy gap of the system or when it is much larger than the maximum energy gap. As an example, consider a particle colliding with a two-level system with energy gap $\Delta > 0$. For simplicity, we consider a spatially symmetric potential $\hat{V}(\hat{x}) = V(-\hat{x})$ in which case the scattering process is independent of the initial direction of the particle α [2,20] and we omit this label. The relevant quantities in Eq. (10) then read exactly $\langle W\rangle(E_p) = (\Delta/2)\cosh^{-1}(\beta\Delta/2)[P_{10}(E_p + e_0)e^{\beta\Delta/2} - P_{01}(E_p + e_1)e^{-\beta\Delta/2}]$ and $\eta(E_p) = \tanh(\beta\Delta/2)[P_{01}(E_p + e_1) - P_{10}(E_p + e_0)]$, where $|1\rangle$ and $|0\rangle$ are the excited and ground state.

At low kinetic energies $0 \leq E_p < \Delta$ we see that Eq. (10) allows for energy extraction from the system (Fig. 2, upper panel). This is because system excitation is forbidden when the particle has an initial kinetic energy lower than the gap: the excitation channel is closed, i.e., $P_{10}(E_p + e_0) = 0$ for $0 \leq E_p < \Delta$. In contrast, a system initially at finite temperature has a nonzero probability to be excited and then relax in the collision: the relaxation channel is always open,

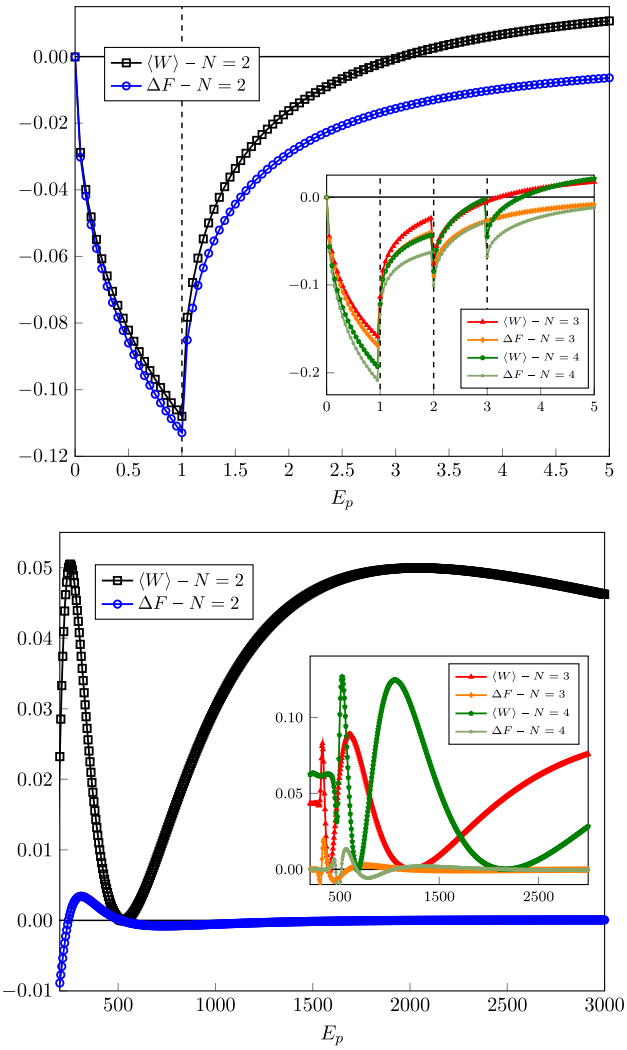

FIG. 2. Average system energy change and lower bound in Eq. (10) at low and high kinetic energies (upper and lower panel, respectively). The explicit dependence of these quantities on E_p was removed in the labels for simplicity. We consider a two-level ($N = 2$) system $\hat{H}_S = (\Delta/2)\hat{\sigma}_z$ and scattering potential $\hat{V}(\hat{x}) = (V_0\pi/2)\hat{\sigma}_x \otimes \cos(\pi\hat{x}/a)$, where Δ is the energy gap, $\hat{\sigma}_{z,x}$ are Pauli matrices, and V_0, a are the energy and length of the potential. The insets show the results when we add one and two more levels ($N = 3$ and $N = 4$), where the energies of the new levels are chosen such that the set of gaps for an N-level system is $\{\Delta, 2\Delta, \ldots, (N-1)\Delta\}$; the interaction in the insets is $\hat{V}(\hat{x}) = (V_0\pi/2)\hat{V} \otimes \cos(\pi\hat{x}/a)$ with $\hat{V}$ having 0's in the diagonal and 1's everywhere else. The scattering matrix is found by solving numerically the multichannel scattering equations [20,63]. The parameters shown are $\Delta = m = a = 1$, $\beta = 0.1$, $V_0 = 100$ and the vertical dashed line in the upper panel indicates $E_p = \Delta, 2\Delta, \ldots, (N-1)\Delta$.

i.e., $P_{01}(E_p + e_1) \geq 0$ for $E_p \geq 0$. In this regime, we can then write $\langle W \rangle(E_p) = -\Delta f(\beta\Delta) P_{01}(E_p + e_1) \leq 0$, where $f(x) = (1 + e^x)^{-1}$ is the Fermi function and $\eta(E_p) = \tanh(\beta\Delta/2) P_{01}(E_p + e_1) \geq 0$. Thus, the maximum energy that can be extracted from a two-level system in any scattering process is $\langle W \rangle_{\text{ext}}^{\max} = \Delta f(\beta\Delta)$. Note when both channels are open, energy can still be extracted in the range $\Delta \leq E_p \leq E_p^{\max}$ where $E_p^{\max}$ is implicitly defined by $\langle W \rangle(E_p^{\max}) = 0$. Similar conclusions can be drawn for an N-level system at low kinetic energies, with different expressions for $\langle W \rangle(E_p)$ and $\eta(E_p)$, provided that we consider the minimum energy gap of the system. These were confirmed numerically (see inset in upper panel of Fig. 2), where it is evident that a larger number of levels allows for more energy extraction at low energies. A systematic study of energy extraction for larger (many-body) systems is left for future work.

At high kinetic energies $E_p \gg \Delta$ energy extraction becomes impossible and we recover unital dynamics (Fig. 2, lower panel). Since in this regime $\eta(E_p) \to 0$, the signature of unital dynamics is $P_{01}(E_p + e_1) = P_{10}(E_p + e_0)$ and we can write $\langle W \rangle(E_p) = \Delta \tanh(\beta\Delta/2) P_{10}(E_p + e_0) \geq 0$. The maximum energy consumed by the two-level system in any scattering process can never exceed $\langle W \rangle_{\text{cons}}^{\max} = \Delta \tanh(\beta\Delta/2)$. In fact, the convergence toward unitality at high kinetic energies is a universal feature of the scattering process, where the behavior of the scattering matrix is mainly determined by the kinetic energy and depends weakly on the system energy gaps $P_{10}(E_p + e_0) = P_{10}(E_p + e_1 - \Delta) \simeq P_{10}(E_p + e_1) = P_{01}(E_p + e_1)$, where the last equality follows from the time-reversal symmetry of the scattering matrix [2,20,24,60]. Similar conclusions hold for an N-level system, with a different expression for $\langle W \rangle(E_p)$, provided that kinetic energy is much larger than the maximum energy gap. These conclusions also hold for nonsymmetric potentials, since at sufficiently high kinetic energies the precise shape of the potential $\hat{V}(\hat{x})$ is not captured by the scattering matrix [23]. We confirmed numerically these predictions for larger system sizes (see inset in lower panel of Fig. 2) and nonsymmetric potentials (not shown).

Note that for a two-level system, the maximum energy that can be extracted $\langle W \rangle_{\text{ext}}^{\max} = \Delta f(\beta\Delta)$ is maximal $\Delta/2$ at $\beta = 0$ (infinite temperature) and decreases monotonically to zero as $\beta \to \infty$ (zero temperature), while the maximum energy consumed $\langle W \rangle_{\text{cons}}^{\max} = \Delta \tanh(\beta\Delta/2)$ is zero at $\beta = 0$ and increases monotonically to Δ at $\beta \to \infty$. Curiously, there is a temperature above which extraction supersedes consumption $0 \leq \beta \leq \beta_0$, where $\beta_0 = \Delta^{-1} \log(2)$ is determined by the intersection of both functions. At this threshold temperature we have $\langle W \rangle_{\text{ext}}^{\max} = \langle W \rangle_{\text{cons}}^{\max} = \Delta/3$.

Conclusions—We have shown how energy fluctuations of a quantum system can be studied within scattering theory beyond the macroscopic source limit. When a collision with a particle pushes the system away from thermal equilibrium, the probability distribution for the energy changes obeys a universal fluctuation relation (8) which allows for energy releasing processes as dictated by nonunital dynamics. Such processes are particularly important if the kinetic energy of the particle is of the order of the energy fluctuations, highlighting the importance of nonunital maps in describing interactions with microscopic sources. At high kinetic energies, unitality is recovered, together with the standard fluctuation theorems for unital dynamics.

Our results may surprise readers familiar with the second law of thermodynamics. As stated by Thomson and Planck, "There is no physical process whose sole effect is energy extraction from a thermal bath." However, we have to note that the state of the particle—generally described by a wave packet—will be distorted in the scattering process [20,24]. In this regard, we show elsewhere that the entropy production, defined as the average log ratio of the probability for the forward process and the backward process, is always positive—even at low kinetic energies, where energy extraction from a thermal system is possible [60]. In addition, we prove that heat fluctuation theorems also follow from (8) when the kinetic energy of the particle is thermally distributed [60]. Our Letter provides a unifying perspective on thermodynamics of quantum systems within a realistic scattering setup.

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