

Work and heat exchanged during sudden quenches of strongly coupled quantum systems

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How should one define thermodynamic quantities (internal energy, work, heat, etc.) for quantum systems coupled to their environments strongly? We examine three definitions, inspired by the literature, of a quantum system's internal energy under strong-coupling conditions. Each internal-energy definition implies a definition of work and a definition of heat. Our study focuses on quenches, common processes in which the Hamiltonian changes abruptly. In these processes, the first law of thermodynamics holds for each set of definitions by construction. However, we prove that only two sets obey the second law. We illustrate our findings using a simple spin model. Our results guide studies of thermodynamic quantities in strongly coupled quantum systems.

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I. INTRODUCTION

Quantum thermodynamics generalizes 19th-century principles about energy processing to quantum systems [1–5]. The field has advanced the studies of thermalization [6,7], fluctuation theorems (extensions of the second law) [8–11], thermal machines [12–14], energetic and informational resources [15,16], and more. Controlled quantum systems have enabled experimental tests of quantum-thermodynamic predictions [14,17–22]. Yet how to define basic quantum-thermodynamic quantities (internal energy, work, heat, etc.) remains an open question [23–42].

A standard thermodynamic setting features two subsystems: a system S of interest and a thermal reservoir R . Typically, S and R satisfy the *weak-coupling assumption*: the subsystems' interaction energy is negligible compared to the system's and reservoir's energies. The total system-reservoir internal energy then approximately equals the sum of the subsystems' internal energies. This decomposition motivates the notion of heat as the energy lost by R and gained by S [43,44].

Macroscopic systems obey the weak-coupling assumption. The reason is that the interaction energy scales as the system-reservoir boundary's surface area, while the system's and reservoir's energies scale with the subsystems' volumes. When S is microscopic, this argument does not apply, and the weak-coupling assumption can break down. The

weak-coupling assumption can break also under long-range interactions between a system's and reservoir's degrees of freedom (DOFs). These examples fall into the *strong-coupling regime*. In this regime, whether the interaction energy should be attributed to S or to R , or somehow split between the two, is unclear [45]. For classical systems, thermodynamic quantities (internal energy, entropy, heat, work, etc.) can nonetheless be defined in the strong-coupling regime consistently with the first and second laws of thermodynamics [46–48].

Several approaches have been proposed for extending the strong-coupling framework into the quantum regime [32,33,36,48–53]. We collate three candidate definitions for internal energy [46,48,54]. Classically, these definitions lead to work and heat definitions that obey the second law. In the quantum case, we prove, only two definitions satisfy the second law; the third definition does not. (All internal-energy, heat, and work quantities in this paper are averages, i.e., expectation values.) Our proof applies to quench processes, in which the Hamiltonian changes abruptly. Such processes enable us to naturally partition the internal-energy change into work and heat. In summary, our results advance quantum thermodynamics by defining quantities consistently with thermodynamic laws.

Our paper is organized as follows: Sections II and III specify the setup and three internal-energy definitions. Section IV describes our quench processes, as well as the partitioning of internal-energy changes into heat and work. Section V identifies the definitions that obey the second law. A spin model illustrates our findings in Sec. VI.

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II. PRELIMINARIES

Consider a finite quantum system $S \cup R$ composed of subsystems S and R . The Hamiltonian of $S \cup R$ is

$$\hat{H}_{SUR} := \hat{H}_S \otimes \hat{\mathbb{1}}_R + \hat{\mathbb{1}}_S \otimes \hat{H}_R + \hat{V}_{SUR}. \quad (1)$$

$\hat{H}_S$ and $\hat{\mathbb{1}}_S$ ($\hat{H}_R$ and $\hat{\mathbb{1}}_R$) act on the Hilbert space of S (R). $\hat{V}_{SUR}$ denotes the interaction between the subsystems. Throughout this paper, we call S the system of interest or the *system*, and we call R the *reservoir*. Also, we use the shorthand $\hat{H}_{SUR} = \hat{H}_S + \hat{H}_R + \hat{V}_{SUR}$.

We denote by $\hat{\rho}_{SUR}$ a state, pure or mixed, of $S \cup R$. The system's reduced state follows from tracing out the reservoir: $\hat{\rho}_S := \text{Tr}_R(\hat{\rho}_{SUR})$. We suppose that the global equilibrium state is the Gibbs state,

$$\hat{\pi}_{SUR} := \frac{e^{-\beta \hat{H}_{SUR}}}{Z_{SUR}}. \quad (2)$$

$\beta := (k_B T)^{-1}$ denotes the inverse temperature; k_B , the Boltzmann factor; and T , the temperature. The partition function is $Z_{SUR} := \text{Tr}_{SR}(e^{-\beta \hat{H}_{SUR}})$. Consequently, the system's equilibrium state is

$$\hat{\pi}_S := \text{Tr}_R(\hat{\pi}_{SUR}) \equiv \frac{e^{-\beta \hat{H}_S^*}}{Z_S^*}. \quad (3)$$

This equation introduces the *Hamiltonian of mean force* [48,49,55–58],

$$\hat{H}_S^* := -\frac{1}{\beta} \ln \left(\frac{\text{Tr}_R(e^{-\beta \hat{H}_{SUR}})}{\text{Tr}_R(e^{-\beta \hat{H}_R})} \right) \quad (4)$$

and partition function $Z_S^* := \text{Tr}_S(e^{-\beta \hat{H}_S^*})$. Throughout this paper, we denote equilibrium states by $\hat{\pi}$, as in Eqs. (2) and (3). We consider thermodynamic processes that begin in the global equilibrium state $\hat{\pi}_{SUR}$.

When $\hat{V}_{SUR}$ is negligible, one can treat $\hat{\pi}_{SUR}$ as a product $\hat{\pi}_S^0 \otimes \hat{\pi}_R^0$ of system and reservoir Gibbs states,

$$\hat{\pi}_S^0 := \frac{e^{-\beta \hat{H}_S}}{Z_S} \quad \text{and} \quad \hat{\pi}_R^0 := \frac{e^{-\beta \hat{H}_R}}{Z_R}, \quad (5)$$

wherein $Z_S := \text{Tr}_S(e^{-\beta \hat{H}_S})$ and $Z_R := \text{Tr}_R(e^{-\beta \hat{H}_R})$. In this *weak-coupling* regime, $\hat{H}_S^* \approx \hat{H}_S$. When $\hat{V}_{SUR}$ is non-negligible, $\hat{H}_S^*$ acts as a modified system Hamiltonian in Eq. (3), capturing the interaction's effects on the system's equilibrium state.

To the equilibrium states $\hat{\pi}_{SUR}$, $\hat{\pi}_S$, and $\hat{\pi}_R^0$, we ascribe the free energies [48]

$$F_{SUR} := -\frac{1}{\beta} \ln(Z_{SUR}), \quad (6)$$

$$F_S := -\frac{1}{\beta} \ln(Z_S^*), \quad (7)$$

and

$$F_R := -\frac{1}{\beta} \ln(Z_R). \quad (8)$$

By the identity $Z_{SUR} = Z_S^* Z_R$ [49,54], Eqs. (6) to (8) imply $F_{SUR} = F_S + F_R$. In this additive relation, all effects of V_{SUR} are bundled into F_S , while F_R does not depend on the system-reservoir interaction. This convention for defining system

and reservoir free energies follows the classical stochastic-thermodynamics literature. There, the convention implies the second law [46,54].

The total internal energy in $\hat{\rho}_{SUR}$ is defined as the expectation value of $\hat{H}_{SUR}$:

$$U_{SUR} := \text{Tr}_{SR}(\hat{H}_{SUR} \hat{\rho}_{SUR}). \quad (9)$$

To state the first and the second laws of thermodynamics, we need also a definition of the system internal energy U_S . If the system-reservoir coupling is strong, the definition of U_S is unclear. The reason is that U_{SUR} does not partition neatly into system and reservoir contributions: part of the total energy resides in the interaction term, which S and R share. In the next section, we discuss three possible definitions of U_S .

III. THREE DEFINITIONS OF INTERNAL ENERGY

We draw three candidate definitions for the system's internal energy, U_S , from the strong-coupling-thermodynamics literature [46–48,54]. These definitions are expressed in terms of expectation values of energy operators, representing the average internal energy of S .

The first definition comes from classical stochastic thermodynamics [46]. The system's internal energy equals the difference between the total internal energy and an isolated reservoir's energy:

$$U_{\text{diff}} := U_{SUR} - U_R^0. \quad (10)$$

$U_R^0 := \text{Tr}_R(\hat{H}_R \hat{\pi}_R^0)$ is the reservoir's equilibrium internal energy in the system's absence. Equation (10) portrays U_R^0 as a fixed reference energy for the reservoir. The remaining energy of $S \cup R$, including contributions from $\hat{V}_{SUR}$, is assigned to S . When $\hat{V}_{SUR}$ is non-negligible, U_{diff} differs from $U_S^0 := \text{Tr}_S(\hat{H}_S \hat{\pi}_S^0)$, the system's equilibrium internal energy in the reservoir's absence.

The second U_S definition portrays $\hat{H}_S^*$ as an effective energy operator. Thus, the system's internal energy is the expectation value of this operator [47,54]:

$$U_{H^*} := \text{Tr}_S(\hat{H}_S^* \hat{\rho}_S). \quad (11)$$

Finally, Refs. [46,48] introduce another effective system Hamiltonian,

$$\hat{E}_S^* := \partial_\beta(\beta \hat{H}_S^*). \quad (12)$$

This operator leads to the third definition of the system's internal energy,

$$U_{E^*} := \text{Tr}_S(\hat{E}_S^* \hat{\rho}_S). \quad (13)$$

In summary, U_{diff} , U_{H^*} , and U_{E^*} represent plausible definitions of the internal energy of a system in any state $\hat{\rho}_S$. These definitions can lead to different internal-energy values. Under certain conditions, however, the definitions are equivalent. We show in Appendix A that $U_{\text{diff}} = U_{H^*} = U_{E^*} = U_S^0$ if two conditions are met: (i) $S \cup R$ is in a Gibbs state, $\hat{\pi}_{SUR}$, and (ii) V_{SUR} is negligible. If (ii) is satisfied but (i) is not, then $U_{H^*} = U_{E^*}$, but both can differ from U_{diff} (Appendix A). Conversely, if (i) is satisfied but (ii) is not, then $U_{\text{diff}} = U_{E^*}$, but both can differ from U_{H^*} (Appendix B) [59].

Later, we focus on processes in which $S \cup R$ begins in a global Gibbs state, $\hat{\pi}_{SUR}$, at a given temperature. This

TABLE I. Overview of system- and interaction-quench processes.

System-quench process		
Time	$\hat{H}_{SUR}(t)$	$\hat{\rho}_S(t)$
$t = 0^-$	$\hat{H}_S^A + \hat{H}_R + \hat{V}_{SUR}$	$\hat{\pi}_S^A$
$t = 0^+$	$\hat{H}_S^B + \hat{H}_R + \hat{V}_{SUR}$	$\hat{\pi}_S^A$
$t = t_f$	$\hat{H}_S^B + \hat{H}_R + \hat{V}_{SUR}$	$\hat{\rho}_S(t_f)$
Interaction-quench process		
Time	$\hat{H}_{SUR}(t)$	$\hat{\rho}_S(t)$
$t = 0^-$	$\hat{H}_S + \hat{H}_R$	$\hat{\pi}_S^A = \hat{\pi}_S^0$
$t = 0^+$	$\hat{H}_S + \hat{H}_R + \hat{V}_{SUR}$	$\hat{\pi}_S^A = \hat{\pi}_S^0$
$t = t_f$	$\hat{H}_S + \hat{H}_R + \hat{V}_{SUR}$	$\hat{\rho}_S(t_f)$

temperature—often the problem’s only well-defined temperature [54]—appears implicitly in the definitions of U_{diff} , U_{H^*} , and U_{E^*} . This approach follows the one in classical stochastic thermodynamics. There, the second law of thermodynamics and variations thereon, for systems driven away from an initial equilibrium state, depend on the initial state’s temperature [60,61].

IV. QUENCH PROCESSES

We now consider quench processes in which $S \cup R$ begins in a global Gibbs state at time $t = 0^-$. Each such process consists of two stages. First, at $t = 0$, a quench occurs: the Hamiltonian, $\hat{H}_{SUR}$, is changed abruptly. Then, from $t = 0^+$ to t_f , $S \cup R$ evolves under the new, fixed, Hamiltonian. The quench process allows us to naturally separate the system’s internal-energy change into work and heat, as we show shortly. Furthermore, quench experiments have verified quantum-thermodynamic predictions [21,62–70], including about nonequilibrium phenomena [65,71–73], quantum ergodicity [74], and quantum phases [75,76].

To describe the quench, we introduce a parameter λ whose value changes from A to B at $t = 0$. We analyze two quench scenarios. In the first, $\hat{H}_{SUR}$ depends on λ through the system Hamiltonian:

$$\hat{H}_{SUR}^\lambda := \hat{H}_S^\lambda + \hat{H}_R + \hat{V}_{SUR}. \quad (14)$$

We call this scenario a *system quench*. In the second scenario, $\hat{H}_{SUR}$ depends on λ through the interaction term:

$$\hat{H}_{SUR} := \hat{H}_S + \hat{H}_R + \lambda \hat{V}_{SUR}. \quad (15)$$

Here, λ changes from $A = 0$ to $B = 1$, turning on the system-reservoir interaction. We call this scenario an *interaction quench*. Table I summarizes, and Fig. 1 illustrates, the two quench processes. These processes involve the following states. The global Gibbs state, relative to the Hamiltonian $\hat{H}_{SUR}^\lambda$, is $\hat{\pi}_{SUR}^\lambda$. The system’s corresponding equilibrium state is

$$\hat{\pi}_S^\lambda := \text{Tr}_R(\hat{\pi}_{SUR}^\lambda) \equiv \frac{e^{-\beta \hat{H}_S^\lambda}}{Z_S^{\lambda}}. \quad (16)$$

At time t , $S \cup R$ and S are in the states $\hat{\rho}_{SUR}(t)$ and $\hat{\rho}_S(t)$, respectively. By assumption, $S \cup R$ begins in equilibrium: $\hat{\rho}_{SUR}(0^-) = \hat{\pi}_{SUR}^A$. In the interaction quench, $\hat{\pi}_{SUR}^A = \hat{\pi}_S^0 \otimes \hat{\pi}_R^0$, wherein Eq. (5) specifies $\hat{\pi}_S^0$ and $\hat{\pi}_R^0$. The state of $S \cup R$

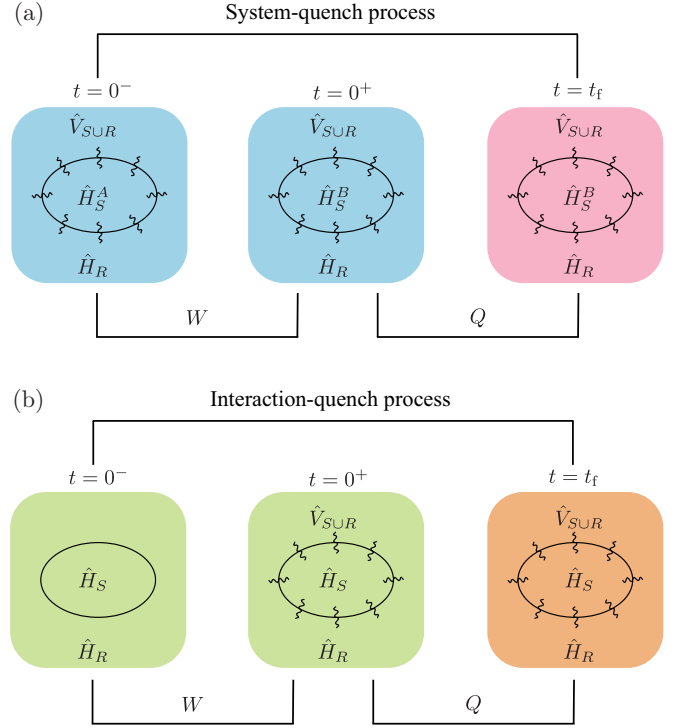


FIG. 1. *Quench processes.* (a) A *system-quench* process begins with a Gibbs state relative to the Hamiltonian $\hat{H}_{SUR} = \hat{H}_S^A + \hat{H}_R + \hat{V}_{SUR}$. The system’s Hamiltonian is quenched to $\hat{H}_S^B$ at $t = 0$. $S \cup R$ then evolves until time t_f . (b) An *interaction-quench* process begins with a separable Gibbs state relative to the Hamiltonian $\hat{H}_{SUR} = \hat{H}_S + \hat{H}_R$. The interaction, $\hat{V}_{SUR}$, is turned on at $t = 0$. In both processes, the quench injects work W into the system. The system absorbs heat Q during the subsequent evolution. A colored box represents $S \cup R$, and a black ellipse encloses S . Identical colors represent identical states. Squiggly lines indicate the interaction, $\hat{V}_{SUR}$.

does not change during either quench, by the sudden approximation [77]:

$$\hat{\rho}_S(0^+) = \hat{\rho}_S(0^-) = \hat{\pi}_S^A. \quad (17)$$

From $t = 0^+$ to t_f , $S \cup R$ evolves under a fixed Hamiltonian: $\hat{H}_{SUR}(t) = \hat{H}_{SUR}^B$. We discuss this evolution at the end of Sec. V.

V. WORK, HEAT, AND THE SECOND LAW

We now identify the work W performed on, and the heat Q absorbed by, the system during a quench process. The three internal-energy definitions (Sec. III) imply corresponding definitions of work and heat. As in classical contexts [46,47,54,79], we determine which definitions satisfy the first and second laws of thermodynamics.

$U_S(t)$ denotes the system’s internal energy at time t , wherein U_S denotes one of the candidate definitions: U_{diff} , U_{H^*} , or U_{E^*} . During a quench process, the system’s internal energy changes by an amount

$$\Delta U_S := U_S(t_f) - U_S(0^-). \quad (18)$$

The first law of thermodynamics attributes the energy change to work and heat:

$$\Delta U_S = W + Q. \quad (19)$$

During the quench, no energy flows between the system and the reservoir, as neither subsystem's state changes. Consequently, S absorbs no heat; any change in the system's internal energy (due to the sudden change in the Hamiltonian) is interpreted as *work*:

$$W := U_S(0^+) - U_S(0^-). \quad (20)$$

After the quench (from $t = 0^+$ to t_f), the state $\hat{\rho}_{SUR}$ evolves under a fixed Hamiltonian, $\hat{H}_{SUR}^B$. The energy transferred between S and R is interpreted as *heat* [61,80]:

$$Q := U_S(t_f) - U_S(0^+). \quad (21)$$

Equations (20) and (21) satisfy the first law [Eq. (19)] by construction. They are motivated by the standard definitions used in weak-coupling quantum thermodynamics [23,80,81].

Different choices for U_S in Eq. (20)— U_{diff} , U_{H^*} , and U_{E^*} —lead to different expressions for the work performed on S :

$$W_{\text{diff}} := \text{Tr}_{SR}([\hat{H}_{SUR}^B - \hat{H}_{SUR}^A] \hat{\pi}_{SUR}^A), \quad (22)$$

$$W_{H^*} := \text{Tr}_S([\hat{H}_S^{*B} - \hat{H}_S^{*A}] \pi_S^A), \quad (23)$$

and

$$W_{E^*} := \text{Tr}_S([\hat{E}_S^{*B} - \hat{E}_S^{*A}] \hat{\pi}_S^A). \quad (24)$$

In each of these definitions, work equals the internal-energy change arising from the sudden change in an energy operator. Equation (22) equates the work performed on S with the work performed on $S \cup R$, consistently with the treatment of $S \cup R$ as one system of interest. If R is much larger than S , however, W_{diff} is often a small difference between two large energies. Additionally, measuring W_{diff} requires access to the S and R degrees of freedom. In these respects, Eqs. (23) and (24) are closer in spirit to the notion of work in classical thermodynamics: to measure work, one does not subtract system-and-reservoir energies.

Similarly, different U_S definitions yield different definitions for the heat absorbed by S :

$$Q_{\text{diff}} := \text{Tr}_{SR}(\hat{H}_{SUR}^B [\hat{\rho}_{SUR}(t_f) - \hat{\pi}_{SUR}^A]), \quad (25)$$

$$Q_{H^*} := \text{Tr}_S(\hat{H}_S^{*B} [\hat{\rho}_S(t_f) - \hat{\pi}_S^A]), \quad (26)$$

and

$$Q_{E^*} := \text{Tr}_S(\hat{E}_S^{*B} [\hat{\rho}_S(t_f) - \hat{\pi}_S^A]). \quad (27)$$

In classical thermodynamics, heat is the energy exchanged by S and R during the change in S 's state. Equations (26) and (27) are consistent with this notion, whereas Eq. (25) is not. If $S \cup R$ is isolated, Eq. (25) implies $Q_{\text{diff}} = 0$, even though S and R can exchange energy throughout the time interval $t \in (0, t_f]$. Thus, representing S 's energy with U_{diff} may preclude a heat definition that simultaneously satisfies the first law and represents heat as the energy exchanged by S and R [82].

In summary, all three sets of work [Eqs. (22)–(24)] and heat definitions [Eqs. (25)–(27)] satisfy the first law by construction: within each set, work plus heat equals the corresponding

internal-energy change. We now identify which definitions obey the second law.

To state the second law, we introduce further notation. Denote by $F_S^A := -\beta^{-1} \ln Z_S^{A*}$ the free energy of S in the equilibrium state relative to the initial Hamiltonian. Define F_S^B analogously relative to the final Hamiltonian. Because S begins in the equilibrium state $\hat{\pi}_S^A$, the second law of thermodynamics assumes the form [83]

$$W \geq \Delta F_S, \quad (28)$$

wherein $\Delta F_S := F_S^B - F_S^A$. In classical thermodynamics, Eq. (28) is the statement of the second law for a system in contact with one thermal reservoir [44]. Equation (28) remains valid even under strong system-reservoir coupling [46,47], and even if S does not end in equilibrium [60]. Rearranging Eq. (28) yields $W - \Delta F_S \geq 0$. The greater the *dissipated work* $W - \Delta F_S$, the more irreversible the process [61].

We now show that two work definitions [Eqs. (22) and (23)] satisfy the second law. In each case, we calculate $W - \Delta F_S$ and prove the inequality in Eq. (28). First consider W_{diff} :

$$\begin{aligned} \beta(W_{\text{diff}} - \Delta F_S) &= \beta\{\text{Tr}_{SR}([\hat{H}_{SUR}^B - \hat{H}_{SUR}^A] \hat{\pi}_{SUR}^A) - (F_S^B - F_S^A)\} \quad (29a) \\ &= \text{Tr}_{SR}(\{\beta[\hat{H}_{SUR}^B - F_{SUR}^B] - \beta[\hat{H}_{SUR}^A - F_{SUR}^A]\} \hat{\pi}_{SUR}^A) \quad (29b) \end{aligned}$$

$$= \text{Tr}_{SR}([\ln \hat{\pi}_{SUR}^A - \ln \hat{\pi}_{SUR}^B] \hat{\pi}_{SUR}^A) \geq 0. \quad (29c)$$

Equation (29b) follows from $F_{SUR} = F_S + F_R$ [from below Eqs. (6) to (8)] and from $\text{Tr}_{SR}(\hat{\pi}_{SUR}^{A/B}) = 1$; the equality in Eq. (29c), from $\hat{\pi}_{SUR} = e^{-\beta(\hat{H}_{SUR} - F_{SUR})}$; and the inequality, from the quantum relative entropy's non-negativity [84]. Similarly, for W_{H^*} ,

$$\begin{aligned} \beta(W_{H^*} - \Delta F_S) &= \beta\{\text{Tr}_S([\hat{H}_S^{*B} - \hat{H}_S^{*A}] \pi_S^A) - (F_S^B - F_S^A)\} \quad (30a) \\ &= \text{Tr}_S(\{\beta[\hat{H}_S^{*B} - F_S^B] - \beta[\hat{H}_S^{*A} - F_S^A]\} \pi_S^A) \quad (30b) \end{aligned}$$

$$= \text{Tr}_S([\ln \hat{\pi}_S^A - \ln \hat{\pi}_S^B] \pi_S^A) \geq 0. \quad (30c)$$

The equality in Eq. (30c) follows from $\hat{\pi}_S = e^{-\beta(\hat{H}_S^* - F_S)}$. We lack an analogous derivation for W_{E^*} , and Sec. VI illustrates numerically that W_{E^*} can violate Eq. (28) [88]. Thus, of the three quantum work definitions, only W_{diff} and W_{H^*} satisfy the second law for our quench processes.

The values of W_{diff} , W_{H^*} , and W_{E^*} can differ. For system quenches, however, we show in Appendix C that, if

$$[\hat{H}_S^A, \hat{V}_{SUR}] = [\hat{H}_S^B, \hat{V}_{SUR}] = 0, \quad (31)$$

then

$$W_{\text{diff}} = W_{H^*} = W_{E^*}. \quad (32)$$

For classical systems undergoing system quenches, W_{diff} , W_{H^*} , and W_{E^*} are identical [46,47].

If the system begins and ends in equilibrium, one can express the second law in terms of heat and entropy. Define the (thermal) entropy of an equilibrium state $\hat{\pi}_S$ [Eq. (3)] using the thermodynamic relation

$$S := \beta(U_S - F_S). \quad (33)$$

U_S evaluates to U_{diff} , U_{H^*} , or U_{E^*} ; and Eq. (7) specifies F_S . Suppose S ends in an equilibrium state at inverse temperature β ,

$$\hat{\rho}_S(t_f) = \hat{\pi}_S^B. \quad (34)$$

Equation (33), with the first law [Eq. (19)], implies that $W - \Delta F_S = \beta^{-1} \Delta S - Q$. Hence the second law [Eq. (28)] is equivalent to

$$Q \leq \beta^{-1} \Delta S. \quad (35)$$

Since Eqs. (28) and (35) are equivalent when S ends in equilibrium, Eqs. (29) and (30) imply

$$Q_{\text{diff}} \leq \beta^{-1} \Delta S_{\text{diff}} \quad (36)$$

and

$$Q_{H^*} \leq \beta^{-1} \Delta S_{H^*}, \quad (37)$$

respectively. We show numerically in Sec. VI that Q_{E^*} can violate Eq. (35).

We derived Eqs. (36) and (37) by assuming that S ends in the equilibrium state $\hat{\pi}_S^B$ [Eq. (34)]. At least two realistic scenarios motivate this assumption:

(1) Suppose that $S \cup R$ is a closed quantum system evolving unitarily under $\hat{H}_{S \cup R}^B$. Let $S \cup R$ satisfy the eigenstate thermalization hypothesis [89], and let R have a thermal reservoir's generic properties: macroscopically many DOFs and a heat capacity much greater than the system's. For sufficiently large t_f , one expects $S \cup R$ to equilibrate to a temperature essentially identical to the initial temperature, β^{-1} . In this case, S ends in the state $\hat{\pi}_S^B$.

(2) Suppose that $S \cup R$ couples weakly to a much larger, thermal *super-reservoir* at a temperature β^{-1} . If t_f is sufficiently large, then $S \cup R$ relaxes to the global Gibbs state $\hat{\pi}_{S \cup R}^B$, which implies Eq. (34).

VI. TWO-SPIN MODEL

A simple, illustrative model features spins S and R . Denote by σ_a^i the Pauli operator with $a \in \{S, R\}$ and $i \in \{x, z\}$. The spins evolve under the Hamiltonian

$$\hat{H}_{S \cup R} = \frac{\epsilon}{2} \sigma_S^z + \frac{\alpha}{2} \sigma_R^z + \gamma \sigma_S^z \sigma_R^z + \chi \sigma_S^x \sigma_R^x, \quad (38)$$

wherein γ and χ denote coupling strengths. Treating one spin as a reservoir may seem odd. In previous sections, however, we did not assume that R contains many degrees of freedom. The Hamiltonian (38) has the form in Eq. (1) and enables us to calculate work and heat analytically.

We assume $S \cup R$ couples weakly to a thermal super-reservoir at a temperature β^{-1} . Moreover, we assume t_f is sufficiently large for $S \cup R$ to equilibrate with the super-reservoir, postquench. (We do not model the super-reservoir explicitly.) These assumptions realize scenario (ii), sketched at the end of Sec. V. We compute the work, heat, free-energy change, and entropy change relevant to each quench described in Table I. Appendix D lists analytical expressions for these quantities. Here, we illustrate the conclusions of Sec. V by evaluating these expressions at specific ϵ , α , γ and χ values. Throughout this section, $\beta = 1$.

During a system quench, $\hat{H}_S := \frac{\epsilon}{2} \sigma_S^z$ changes abruptly: ϵ switches from $\epsilon_A = 0$ to ϵ_B . α , γ , and χ remain fixed. Figure 2(a) displays the dissipated work, $W - \Delta F_S$, as a function of ϵ_B . W_{diff} and W_{H^*} satisfy the second law, in agreement with Eqs. (29) and (30). In contrast, W_{E^*} violates the second law at certain ϵ_B values. These conclusions hold also if ϵ_A is nonzero.

During an interaction quench, γ and χ change suddenly from $\gamma_A = \chi_A = 0$ to γ_B and χ_B . Figure 2(b) displays the dissipated work as a function of γ_B . The other parameters remain fixed. Again, W_{diff} and W_{H^*} satisfy the second law. However, W_{E^*} violates it at some γ_B values.

Turning to Fig. 2(c), we return to the system quench. However, we now set $\chi = 0$ in Eq. (38), to satisfy the commutation relations in Eqs. (31). In agreement with Eq. (32), the three dissipated-work quantities equal each other. Additionally, they obey the second law.

Strong-coupling quantum thermodynamics naturally applies to lattice gauge theories, as proposed in Ref. [90]. Gauge theories and their lattice formulations are crucial to high-energy and nuclear physics [91,92], condensed and synthetic quantum matter [93–96], and quantum information science [97–104]. Local constraints among DOFs define lattice gauge theories. Physical systems can only be in states consistent with those constraints. A slight modification converts our two-spin model into a simple lattice gauge theory. We introduce an LGT-type constraint by setting $k = -\gamma > 0$ and adding a term $k \mathbb{1}_{S \cup R}$ to $\hat{H}_{S \cup R}$ in Eq. (38):

$$\hat{H}_{S \cup R} = \frac{\epsilon}{2} \sigma_S^z + \frac{\alpha}{2} \sigma_R^z + \chi \sigma_S^x \sigma_R^x + k (\mathbb{1}_{S \cup R} - \sigma_S^z \sigma_R^z). \quad (39)$$

In the limit as $k \rightarrow \infty$ (at a fixed, finite temperature), the last term acts as an energy penalty: it constrains the system to the eigenvalue-1 eigenspace of $\sigma_S^z \sigma_R^z$. This operator serves as a *Gauss-law operator*. It specifies which states satisfy the constraint. Since the interactions in Eq. (39) are non-negligible, strong-coupling quantum thermodynamics applies to this model, as to other lattice gauge theories [90]. To test our results, we subject the two-spin model Eq. (39) (with $k \rightarrow \infty$) to the system-quench process [Fig. 2(a)] [105]. We find that W_{diff} and W_{H^*} satisfy the second law, whereas W_{E^*} does not [see Appendix D].

VII. DISCUSSION AND OUTLOOK

We have scrutinized definitions of thermodynamic properties of strongly coupled quantum systems. We compared three definitions of the system's internal energy— U_{diff} , U_{H^*} , and U_{E^*} [Eqs. (10), (11), and (13)]—during quench processes. All three lead to work and heat definitions that satisfy the first law of thermodynamics, by construction. However, we found, only the definitions based on U_{diff} and U_{H^*} satisfy the second law. These conclusions hold independently of the final states when the second law is expressed in terms of work and free energy. If the system equilibrates after the quench, the same conclusions hold when the second law is expressed in terms of heat and entropy. We illustrated these general results with a simple model of two coupled spins. These conclusions distinguish quantum from classical thermodynamics. Our work can therefore guide the thermodynamics of strongly coupled quantum systems of relevance to condensed matter,

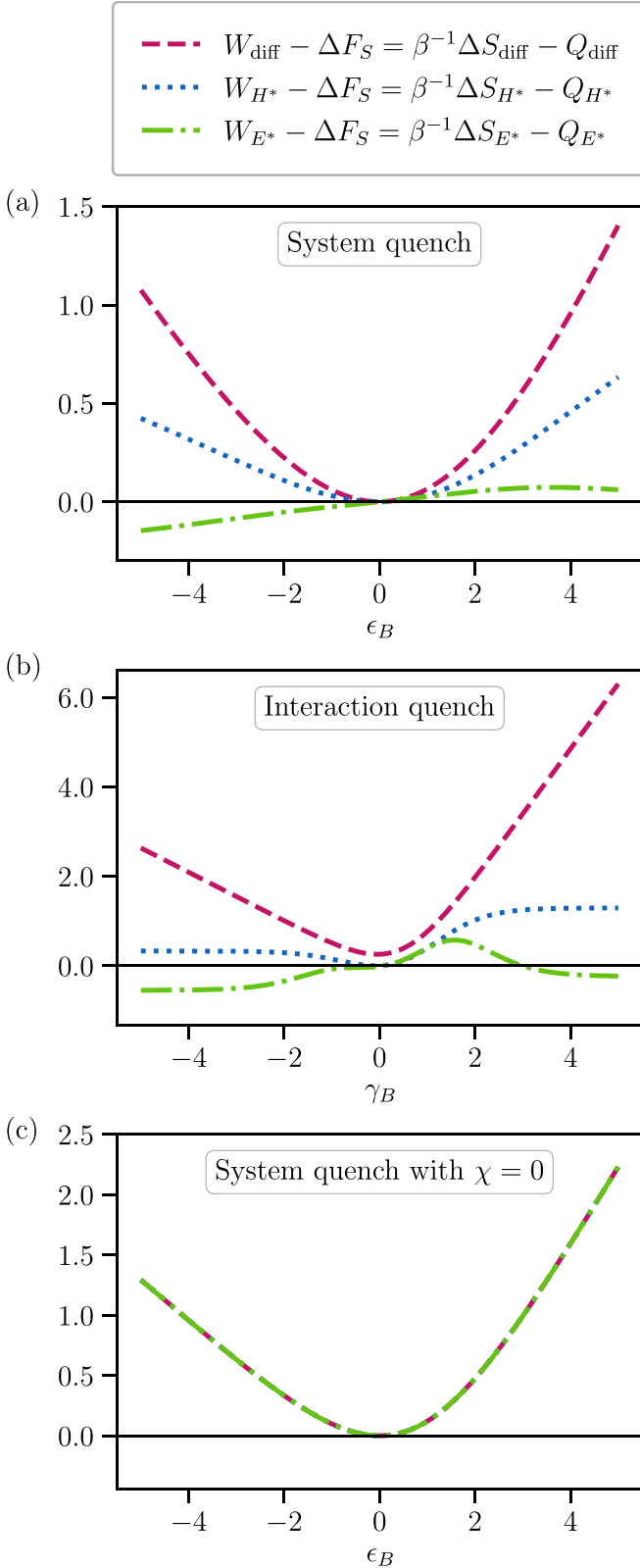


FIG. 2. *Thermodynamic quantities of the two-spin model.* (a) During a system quench, the ϵ in Eq. (38) changes from $\epsilon_A = 0$ to ϵ_B . The dissipated work is plotted as a function of ϵ_B , with $\alpha = 0.8$, $\gamma = 1.2$, and $\chi = 1.8$. W_{diff} and W_{H^*} satisfy the second law [Eq. (28)]; consequently, so do Q_{diff} and Q_{H^*} [Eq. (35)]. W_{E^*} and Q_{E^*} do not. (b) During an interaction quench, the coupling constants

high-energy and nuclear physics, quantum chemistry, and quantum error correction (see, e.g., Refs. [90,106–108]).

This work opens the door to further opportunities:

(a) We focused on quench processes because they allow for naturally partitioning the system’s internal-energy change into work and heat, even when the system and reservoir couple strongly. Our results may extend to thermodynamic processes beyond quenches, where the partitioning is less clear. Examples include quantum-adiabatic processes, used to prepare quantum states in quantum simulations, and particle collisions, relevant to hydrodynamics [109] and nuclear and high-energy physics [90,110,111].

(b) In this work, we have defined average work and heat quantities. One can define classical work and heat as fluctuating quantities, whose values differ from realization to realization of a process. Fluctuation theorems (extensions of the second law), derived in this setting [46,47,54,55,60,79,112–119], have been extended to strong system-reservoir couplings [46,47,54,55]. Can one define fluctuating work and heat exchanged within strongly coupled quantum systems? For example, the two-point-measurement definition of work supports a fluctuation theorem for closed quantum systems [8–10,25,58,120,121]. One can apply this scheme in strong-coupling contexts by treating $S \cup R$ as a closed quantum system. Yet can one infer the fluctuating work performed on S from measurements of S alone?

(c) Of the two internal-energy definitions that obey the second law, one [Eq. (11)] stems from the Hamiltonian of mean force, $\hat{H}_S^*$ [Eq. (4)]. This operator is related to the system’s entanglement Hamiltonian if $S \cup R$ is in equilibrium [90]. Entanglement-Hamiltonian tomography enables efficient experimental measurements, or numerical determinations, of a subsystem’s quantum state [122–126]. Such tomography has been applied to ground, excited, and nonequilibrium states of isolated systems [62,127–133]. Future work will extend entanglement-Hamiltonian tomography to thermal states. This extension will allow one to access thermodynamic quantities in the strong-coupling regime of quantum simulations.

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γ and χ change from $\gamma_A = \chi_A = 0$ to γ_B and χ_B . Dissipated work is plotted as a function of γ_B , with $\epsilon = 1.0$, $\alpha = 5.0$, and $\chi_B = 1.2$. Qualitatively similar results follow from plotting the dissipated work as a function of χ_B at fixed ϵ , α , and γ_B . (c) We set $\chi = 0$ in Eq. (38), such that $\hat{H}_S$ commutes with $\hat{V}_{S \cup R}$ before and after the quench [Eqs. (31)]. The work dissipated during a system quench is plotted as a function of ϵ_B , with fixed $\epsilon_A = 0$, $\alpha = 0.8$, and $\gamma = 1.2$. The three curves coincide, as expected [Eq. (32)].

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX A: WEAK-COUPLING LIMIT

In the weak-coupling limit, the interactions between S and R , while nonvanishing, are small enough to be neglected in calculations of partition functions and free energies. Therefore, we model the weak-coupling limit by setting $V_{S \cup R} = 0$ in Eq. (1):

$$\hat{H}_{S \cup R} = \hat{H}_S + \hat{H}_R. \quad (\text{A1})$$

In this limit, we demonstrate, the main text’s three internal-energy definitions are equivalent.

Under the assumption in Eq. (A1), one obtains

$$\hat{H}_S^* := -\frac{1}{\beta} \ln \left(\frac{\text{Tr}_R(e^{-\beta(\hat{H}_S + \hat{H}_R)})}{\text{Tr}_R(e^{-\beta\hat{H}_R})} \right) = -\frac{1}{\beta} \ln(e^{-\beta\hat{H}_S}) = \hat{H}_S \quad (\text{A2})$$

and

$$\hat{E}_S^* := \partial_\beta(\beta\hat{H}_S^*) = \partial_\beta(\beta\hat{H}_S) = \hat{H}_S. \quad (\text{A3})$$

Thus, both $\hat{H}_S^*$ and $\hat{E}_S^*$ reduce to the system Hamiltonian $\hat{H}_S$ in the weak-coupling limit. Consequently, by Eqs. (11) and (13),

$$U_{H^*} = U_{E^*} = \text{Tr}_S(\hat{H}_S \hat{\rho}_S), \quad (\text{A4})$$

for any state $\hat{\rho}_S$.

We now additionally assume that $S \cup R$ is in a global Gibbs state. As a result, $\hat{\rho}_S = \hat{\pi}_S^0$, $U_{H^*} = U_{E^*} = U_S^0$, and

$$U_{\text{diff}} = \text{Tr}_{SR}([\hat{H}_S \otimes \hat{\mathbb{1}}_R + \hat{\mathbb{1}}_S \otimes \hat{H}_R][\hat{\pi}_S^0 \otimes \hat{\pi}_R^0]) - \text{Tr}_R(\hat{H}_R \hat{\pi}_R^0) \quad (\text{A5a})$$

$$= \text{Tr}_S(\hat{H}_S \hat{\pi}_S^0) + \text{Tr}_R(\hat{H}_R \hat{\pi}_R^0) - \text{Tr}_R(\hat{H}_R \hat{\pi}_R^0) \quad (\text{A5b})$$

$$= \text{Tr}_S(\hat{H}_S \hat{\pi}_S^0) = U_S^0. \quad (\text{A5c})$$

Thus,

$$U_{\text{diff}} = U_{H^*} = U_{E^*} = U_S^0. \quad (\text{A6})$$

Three internal-energy definitions would be equivalent in the weak-coupling limit if one defined U_{diff} differently from Eq. (10). Define $U_R := \text{Tr}_R(\hat{H}_R \rho_R)$ and $\tilde{U}_{\text{diff}} := U_{S \cup R} - U_R$. If $\rho_{S \cup R}$ is any product state $\rho_S \otimes \rho_R$, then $\tilde{U}_{\text{diff}} = U_{H^*} = U_{E^*}$. Since $\tilde{U}_{\text{diff}}$ is nonstandard, we use Eq. (10) in this manuscript.

APPENDIX B: EQUIVALENCE OF U_{diff} AND U_{E^*} WHEN $S \cup R$ IS IN A GLOBAL GIBBS STATE

In this appendix, we show that $U_{E^*} = U_{\text{diff}}$ when $S \cup R$ is in a global Gibbs state. The classical analog was proved in Ref. [46], then used in Ref. [48] to derive quantum fluctuation theorems. We do not assume, in this appendix, that the coupling is weak.

We begin by rewriting Eq. (12):

$$\hat{E}_S^* = \partial_\beta(\beta\hat{H}_S^*) \quad (\text{B1a})$$

$$= \partial_\beta \left[-\ln \left(\frac{\text{Tr}_R(e^{-\beta\hat{H}_{S \cup R}})}{\text{Tr}_R(e^{-\beta\hat{H}_R})} \right) \right] \quad (\text{B1b})$$

$$= -\frac{\partial_\beta[\text{Tr}_R(e^{-\beta\hat{H}_{S \cup R}})]}{\text{Tr}_R(e^{-\beta\hat{H}_{S \cup R}})} + \frac{\partial_\beta[\text{Tr}_R(e^{-\beta\hat{H}_R})]}{\text{Tr}_R(e^{-\beta\hat{H}_R})}. \quad (\text{B1c})$$

Consider applying the derivative’s definition to the first term:

$$\begin{aligned} \partial_\beta[\text{Tr}_R(e^{-\beta\hat{H}_{S \cup R}})] &= \lim_{\delta\beta \rightarrow 0} \frac{\text{Tr}_R(e^{-(\beta+\delta\beta)\hat{H}_{S \cup R}}) - \text{Tr}_R(e^{-\beta\hat{H}_{S \cup R}})}{\delta\beta} \quad (\text{B2a}) \\ &= \lim_{\delta\beta \rightarrow 0} \text{Tr}_R \left(e^{-\beta\hat{H}_{S \cup R}} \frac{(e^{-\delta\beta\hat{H}_{S \cup R}} - 1)}{\delta\beta} \right) \quad (\text{B2b}) \\ &= -\text{Tr}_R(\hat{H}_{S \cup R} e^{-\beta\hat{H}_{S \cup R}}). \quad (\text{B2c}) \end{aligned}$$

The final term in Eqs. (B1) simplifies similarly. Therefore,

$$\hat{E}_S^* = \frac{\text{Tr}_R(\hat{H}_{S \cup R} e^{-\beta\hat{H}_{S \cup R}})}{\text{Tr}_R(e^{-\beta\hat{H}_{S \cup R}})} - \frac{\text{Tr}_R(\hat{H}_R e^{-\beta\hat{H}_R})}{\text{Tr}_R(e^{-\beta\hat{H}_R})}. \quad (\text{B3})$$

To calculate U_{E^*} , one takes the expectation value of $\hat{E}_S^*$ in the state $\hat{\pi}_S$:

$$U_{E^*} = \text{Tr}_S(\hat{E}_S^* \hat{\pi}_S). \quad (\text{B4})$$

Substituting $\hat{\pi}_S = \text{Tr}_R(\hat{\pi}_{SUR})$, and $\hat{E}_S^*$ from Eq. (B3), gives

$$U_{E^*} = \frac{1}{Z_{SUR}} \text{Tr}_S(\text{Tr}_R(\hat{H}_{SUR} e^{-\beta \hat{H}_{SUR}})) - \frac{1}{Z_R} \text{Tr}_S(\hat{\pi}_S \text{Tr}_R(\hat{H}_R e^{-\beta \hat{H}_R})). \quad (\text{B5})$$

By distributing and evaluating the traces, one obtains

$$U_{E^*} = \text{Tr}_{SR}(\hat{H}_{SUR} \hat{\pi}_{SUR}) - \text{Tr}_S(\hat{\pi}_S) \text{Tr}_R(\hat{H}_R \hat{\pi}_R) \quad (\text{B6a})$$

$$= \text{Tr}_{SR}(\hat{H}_{SUR} \hat{\pi}_{SUR}) - U_R^0. \quad (\text{B6b})$$

Therefore, when $\hat{\rho}_{SUR} = \hat{\pi}_{SUR}$,

$$U_{E^*} = U_{\text{diff}}. \quad (\text{B7})$$

APPENDIX C: OPERATOR COMMUTATIVITY AND EQUAL WORK QUANTITIES IN A SYSTEM QUENCH

In this appendix, we show that the commutation relations in Eqs. (31) suffice for establishing the equalities $W_{\text{diff}} = W_{H^*} = W_{E^*}$ for a system quench. We motivate these equalities by observing that the corresponding classical work definitions are equivalent (for a system quench) [47], and that the commutation of observables under multiplication is often a signal of classicality.

Recall that a system-quench process proceeds as follows. $S \cup R$ begins in the Gibbs state $\hat{\pi}_{SUR}^A$ at $t = 0^-$. At $t = 0$, one quenches the system Hamiltonian from $\hat{H}_S^A$ to $\hat{H}_S^B$. From $t = 0^+$ to t_f , $S \cup R$ evolves under $\hat{H}_{SUR}^B$.

First, we show that $W_{\text{diff}} = W_{H^*}$ if the commutation relations (31) hold. Substituting the $\hat{H}_S^*$ definition [Eq. (4)] into the W_{H^*} definition [Eq. (23)], one obtains

$$W_{H^*} = -\frac{1}{\beta} \text{Tr}_S(\ln(\text{Tr}_R(e^{-\beta \hat{H}_{SUR}^B})) \hat{\pi}_S^A) + \frac{1}{\beta} \text{Tr}_S(\ln(\text{Tr}_R(e^{-\beta \hat{H}_{SUR}^A})) \hat{\pi}_S^A). \quad (\text{C1})$$

The expression simplifies because $\hat{H}_S^A$ and $\hat{H}_S^B$ commute with $\hat{V}_{SUR}$:

$$\begin{aligned} W_{H^*} &= -\frac{1}{\beta} \text{Tr}_S(\ln(e^{-\beta \hat{H}_S^B} \text{Tr}_R(e^{-\beta(\hat{H}_R + \hat{V}_{SUR})})) \hat{\pi}_S^A) \\ &\quad + \frac{1}{\beta} \text{Tr}_S(\ln(e^{-\beta \hat{H}_S^A} \text{Tr}_R(e^{-\beta(\hat{H}_R + \hat{V}_{SUR})})) \hat{\pi}_S^A) \quad (\text{C2a}) \\ &= -\frac{1}{\beta} \text{Tr}_S(\ln(e^{-\beta \hat{H}_S^B}) \hat{\pi}_S^A) \\ &\quad + \frac{1}{\beta} \text{Tr}_S(\ln(e^{-\beta \hat{H}_S^A}) \hat{\pi}_S^A). \quad (\text{C2b}) \end{aligned}$$

We substitute $\hat{\pi}_S^A = \text{Tr}_R(\hat{\pi}_{SUR}^A)$, rearrange the traces, and recall that $\hat{H}_S^B - \hat{H}_S^A = \hat{H}_{SUR}^B - \hat{H}_{SUR}^A$:

$$W_{H^*} = \text{Tr}_{SR}([\hat{H}_{SUR}^B - \hat{H}_{SUR}^A] \hat{\pi}_{SUR}^A) = W_{\text{diff}}. \quad (\text{C3})$$

To obtain a similar expression for W_{E^*} , we apply the definitions of $\hat{H}_S^*$ [Eq. (4)] and $\hat{E}_S^*$ [Eq. (12)], as well as the commutation relations [Eqs. (31)]. The difference $\hat{E}_S^{*B} - \hat{E}_S^{*A}$ becomes

$$\hat{E}_S^{*B} - \hat{E}_S^{*A} = \partial_\beta(\beta \hat{H}_S^{*B} - \beta \hat{H}_S^{*A}) \quad (\text{C4a})$$

$$= -\partial_\beta [\ln(\text{Tr}_R(e^{-\beta \hat{H}_{SUR}^B})) - \ln(\text{Tr}_R(e^{-\beta \hat{H}_{SUR}^A}))] \quad (\text{C4b})$$

$$= -\partial_\beta [\ln(e^{-\beta \hat{H}_S^B} \text{Tr}_R(e^{-\beta(\hat{H}_R + \hat{V}_{SUR})})) - \ln(e^{-\beta \hat{H}_S^A} \text{Tr}_R(e^{-\beta(\hat{H}_R + \hat{V}_{SUR})}))] \quad (\text{C4c})$$

$$= \hat{H}_S^B - \hat{H}_S^A. \quad (\text{C4d})$$

Inserting Eq. (C4d) into Eq. (24), with $\hat{\pi}_S^A = \text{Tr}_R(\hat{\pi}_{SUR}^A)$, gives

$$W_{E^*} = \text{Tr}_{SR}([\hat{H}_{SUR}^B - \hat{H}_{SUR}^A] \hat{\pi}_{SUR}^A) = W_{\text{diff}}. \quad (\text{C5})$$

Thus, $W_{\text{diff}} = W_{H^*} = W_{E^*}$ when a system quench obeys the commutation relations (31). In contrast, even when the commutation relations hold, the three work quantities differ if the interaction term changes abruptly [135]. We speculate that this observation extends to the analogous classical setup.

If $W_{\text{diff}} = W_{H^*} = W_{E^*}$, W_{E^*} satisfies the second law due to Eqs. (30) [and, separately, due to Eqs. (29)]: $W_{E^*} \geq \Delta F_S$.

APPENDIX D: EXPLICIT EXPRESSIONS FOR WORK AND HEAT EXCHANGED IN THE TWO-SPIN MODEL

We analytically derive expressions for the work, heat, entropy, and free energy in the two-spin model of Sec. VI. We use these expressions to generate Fig. 2.

The spin Hamiltonian $\hat{H}_{SUR}$ [Eq. (38)] can be diagonalized easily. In terms of the eigenbasis of $\hat{H}_{SUR}$, the Gibbs state is

$$\hat{\pi}_{SUR} = \frac{1}{Z_{SUR}} \text{diag}(e^{-\beta(\gamma - \eta_+)}, e^{-\beta(\gamma + \eta_+)}, e^{\beta(\gamma + \eta_-)}, e^{\beta(\gamma - \eta_-)}). \quad (\text{D1})$$

We have defined $\eta_\pm := \sqrt{(\frac{\epsilon}{2} \pm \frac{\alpha}{2})^2 + \chi^2}$, where ϵ , α , and χ are the Hamiltonian parameters. The partition function is

$$Z_{SUR} = 2e^{-\beta\gamma} \cosh(\beta\eta_+) + 2e^{\beta\gamma} \cosh(\beta\eta_-). \quad (\text{D2})$$

To calculate the system's thermal state, we trace out the reservoir from $\hat{\pi}_{SUR}$. In terms of the σ_S^z eigenbasis,

$$\hat{\pi}_S = \frac{1}{Z_{SUR}} \begin{pmatrix} X_- & 0 \\ 0 & X_+ \end{pmatrix}, \quad (\text{D3})$$

wherein

$$\begin{aligned} X_\pm &= e^{-\beta\gamma} \left[\cosh(\beta\eta_+) \pm \frac{a_+}{\eta_+} \sinh(\beta\eta_+) \right] \\ &\quad + e^{\beta\gamma} \left[\cosh(\beta\eta_-) \pm \frac{a_-}{\eta_-} \sinh(\beta\eta_-) \right] \quad (\text{D4}) \end{aligned}$$

and $a_\pm = (\epsilon \pm \alpha)/2$. Using the same basis, we also calculate $\hat{H}_S^*$ and $\hat{E}_S^*$:

$$\hat{H}_S^* = -\frac{1}{\beta} \begin{pmatrix} \ln\left(\frac{X_-}{2 \cosh(\frac{\beta\alpha}{2})}\right) & 0 \\ 0 & \ln\left(\frac{X_+}{2 \cosh(\frac{\beta\alpha}{2})}\right) \end{pmatrix}, \quad (\text{D5})$$

and

$$\hat{E}_S^* = \begin{pmatrix} -\frac{\partial_\beta X_-}{X_-} + \frac{\alpha}{2} \tanh\left(\frac{\beta\alpha}{2}\right) & 0 \\ 0 & -\frac{\partial_\beta X_+}{X_+} + \frac{\alpha}{2} \tanh\left(\frac{\beta\alpha}{2}\right) \end{pmatrix}. \quad (\text{D6})$$

1. System quench

During the system quench, the system-Hamiltonian parameter ϵ in Eq. (38) changes from ϵ_A to ϵ_B [see Table I and Fig. 1(a)]. Let us define $\alpha_+^A := \alpha_+|_{\epsilon=\epsilon_A}$. We analogously define other quantities that carry A or B superscripts.

Equations (22)–(24) show the three work definitions. The first evaluates to

$$W_{\text{diff}} = \frac{(\epsilon_A - \epsilon_B)}{Z_{\text{SUR}}^A} \left[\frac{\alpha_+^A}{\eta_+^A} e^{-\beta\gamma} \sinh(\beta\eta_+^A) + \frac{\alpha_-^A}{\eta_-^A} e^{\beta\gamma} \sinh(\beta\eta_-^A) \right]. \quad (\text{D7})$$

We substitute Eqs. (D3) and (D5) into Eq. (23), with superscripts A and B denoting the parameter values ϵ_A and ϵ_B :

$$W_{H^*} = \frac{-1}{\beta Z_{\text{SUR}}^A} \left[X_-^A \ln\left(\frac{X_-^B}{X_-^A}\right) + X_+^A \ln\left(\frac{X_+^B}{X_+^A}\right) \right]. \quad (\text{D8})$$

Analogously, we calculate W_{E^*} using Eqs. (D3), (D6), and (24):

$$W_{E^*} = \frac{1}{Z_{\text{SUR}}^A} \left(\partial_\beta X_-^A - \frac{X_-^A}{X_-^B} \partial_\beta X_-^B + \partial_\beta X_+^A - \frac{X_+^A}{X_+^B} \partial_\beta X_+^B \right). \quad (\text{D9})$$

One can calculate the heat similarly:

$$\begin{aligned} Q_{\text{diff}} = & \frac{1}{Z_{\text{SUR}}^B} \{ 2\gamma [e^{-\beta\gamma} \cosh(\beta\eta_+^B) - e^{\beta\gamma} \cosh(\beta\eta_-^B)] \\ & - 2\eta_+^B e^{-\beta\gamma} \sinh(\beta\eta_+^B) - 2\eta_-^B e^{\beta\gamma} \sinh(\beta\eta_-^B) \} \\ & + \frac{1}{Z_{\text{SUR}}^A} \left\{ 2\gamma [-e^{-\beta\gamma} \cosh(\beta\eta_+^A) + e^{\beta\gamma} \cosh(\beta\eta_-^A)] \right. \\ & + 2e^{-\beta\gamma} \sinh(\beta\eta_+^A) \left(\frac{\alpha_+^B \alpha_+^A + \chi^2}{\eta_+^A} \right) \\ & \left. + 2e^{\beta\gamma} \sinh(\beta\eta_-^A) \left(\frac{\alpha_-^B \alpha_-^A + \chi^2}{\eta_-^A} \right) \right\}, \quad (\text{D10}) \end{aligned}$$

$$Q_{H^*} = \frac{1}{\beta} \left[\left(\frac{X_-^A}{Z_{\text{SUR}}^A} - \frac{X_-^B}{Z_{\text{SUR}}^B} \right) \ln X_-^B + \left(\frac{X_+^A}{Z_{\text{SUR}}^A} - \frac{X_+^B}{Z_{\text{SUR}}^B} \right) \ln X_+^B \right], \quad (\text{D11})$$

and

$$Q_{E^*} = \left(\frac{X_-^A}{Z_{\text{SUR}}^A} - \frac{X_-^B}{Z_{\text{SUR}}^B} \right) \frac{\partial_\beta X_-^B}{X_-^B} + \left(\frac{X_+^A}{Z_{\text{SUR}}^A} - \frac{X_+^B}{Z_{\text{SUR}}^B} \right) \frac{\partial_\beta X_+^B}{X_+^B}. \quad (\text{D12})$$

During a system quench, the system's free energy [Eq. (7)] changes by an amount

$$\Delta F_S = -\frac{1}{\beta} \ln \left(\frac{e^{-\beta\gamma} \cosh(\beta\eta_+^B) + e^{\beta\gamma} \cosh(\beta\eta_-^B)}{e^{-\beta\gamma} \cosh(\beta\eta_+^A) + e^{\beta\gamma} \cosh(\beta\eta_-^A)} \right). \quad (\text{D13})$$

The three internal-energy definitions lead to three entropy definitions via Eq. (33):

$$\begin{aligned} \Delta S_{\text{diff}} = \Delta S_{E^*} = & -\beta \left(\frac{\partial_\beta X_-^B + \partial_\beta X_+^B}{Z_{\text{SUR}}^B} - \frac{\partial_\beta X_-^A + \partial_\beta X_+^A}{Z_{\text{SUR}}^A} \right) \\ & + \ln \left(\frac{Z_{\text{SUR}}^B}{Z_{\text{SUR}}^A} \right), \quad (\text{D14}) \end{aligned}$$

and

$$\begin{aligned} \Delta S_{H^*} = & \frac{X_-^B}{Z_{\text{SUR}}^B} \ln \left(\frac{Z_{\text{SUR}}^B}{X_-^B} \right) - \frac{X_-^A}{Z_{\text{SUR}}^A} \ln \left(\frac{Z_{\text{SUR}}^A}{X_-^A} \right) \\ & + \frac{X_+^B}{Z_{\text{SUR}}^B} \ln \left(\frac{Z_{\text{SUR}}^B}{X_+^B} \right) - \frac{X_+^A}{Z_{\text{SUR}}^A} \ln \left(\frac{Z_{\text{SUR}}^A}{X_+^A} \right). \quad (\text{D15}) \end{aligned}$$

Since $S \cup R$ begins and ends in a Gibbs state, $\Delta U_{\text{diff}} = \Delta U_{E^*}$ implies that $\Delta S_{\text{diff}} = \Delta S_{E^*}$ [Eqs. (33) and (B7)].

2. Interaction quench

During an interaction quench, the system-reservoir interaction changes abruptly [see Table I and Fig. 1(b)]. The coupling parameters, γ and χ , change from zero to γ_B and χ_B at $t = 0$. Subsequently, $S \cup R$ evolves to a Gibbs state of the Hamiltonian $\hat{H}_{\text{SUR}}^B$ [Eq. (38)]. The initial state $\hat{\pi}_S^0 \otimes \hat{\pi}_R^0$ contains the factors

$$\hat{\pi}_S^0 = \frac{1}{2 \cosh(\beta\epsilon/2)} \begin{pmatrix} \epsilon/2 & 0 \\ 0 & -\epsilon/2 \end{pmatrix} \quad (\text{D16})$$

and

$$\hat{\pi}_R^0 = \frac{1}{2 \cosh(\beta\alpha/2)} \begin{pmatrix} \alpha/2 & 0 \\ 0 & -\alpha/2 \end{pmatrix}, \quad (\text{D17})$$

in terms of the σ_S^z and σ_R^z eigenbases, respectively. At $t = 0^-$, S and R do not interact; hence $\gamma_A = \chi_A = 0$, and $\hat{H}_S^{*A} = \hat{E}_S^{*A} = \hat{H}_S^A$ (see Appendix A). When $t > 0$, $\hat{H}_S^{*B}$ and $\hat{E}_S^{*B}$ have the forms in Eqs. (D5) and (D6), with $\gamma_B, \chi_B \neq 0$. Equation (D1) specifies the final $S \cup R$ state, $\hat{\pi}_{\text{SUR}}^B$; and Eq. (D3), the final S state, $\hat{\pi}_S^B$. The final total partition function is

$$Z_{\text{SUR}}^B = 2e^{-\beta\gamma} \cosh(\beta\eta_1) + 2e^{\beta\gamma} \cosh(\beta\eta_2). \quad (\text{D18})$$

Here and below, to prevent clutter, we drop subscripts and denote the coupling parameters by $\gamma_B = \gamma$ and $\chi_B = \chi$. Evaluating Eqs. (22)–(24), we arrive at the following expressions

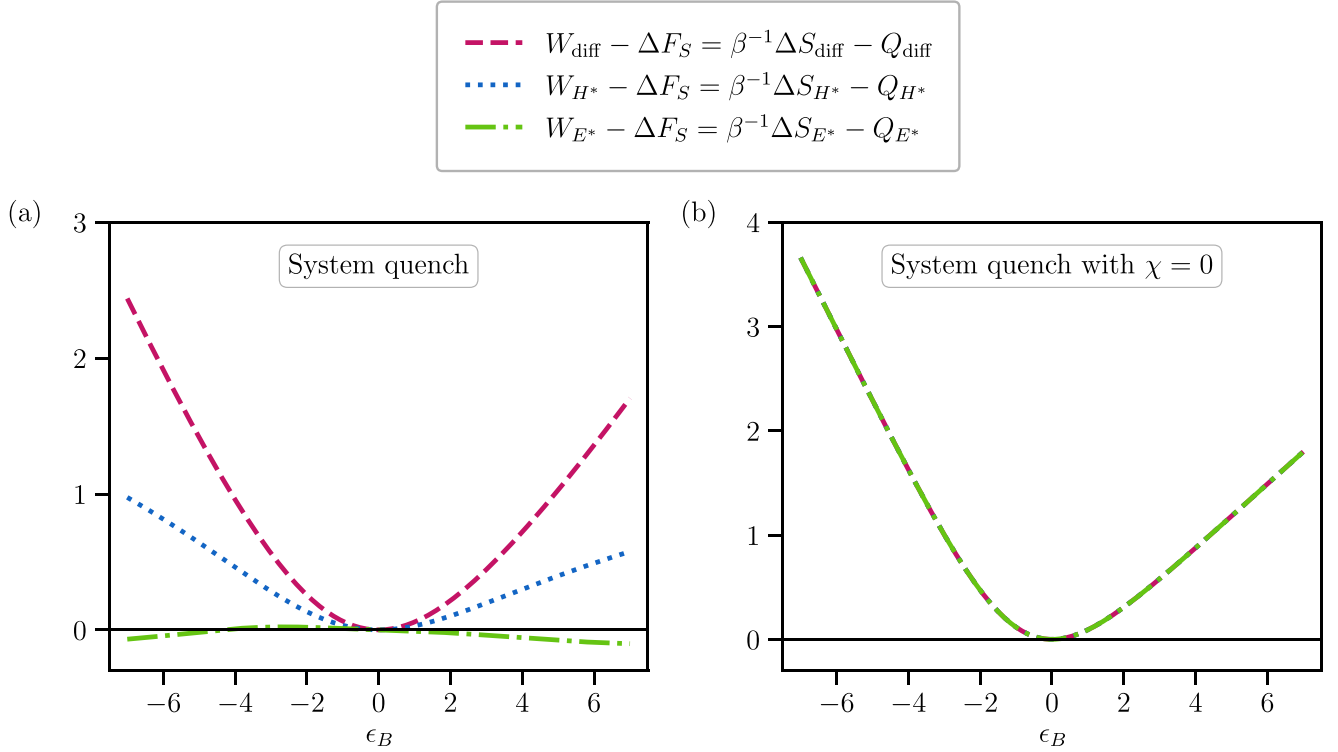


FIG. 3. Thermodynamic quantities of the LGT-type two-spin model undergoing a system-quench process. The ϵ in Eq. (39) changes instantaneously from $\epsilon_A = 0$ to ϵ_B . We fix $\alpha = 0.8$ and $\chi = 1.8$. The dissipated work is plotted as a function of ϵ_B . (a) During a system quench, W_{diff} and W_{H^*} satisfy the second law [Eq. (28)]; consequently, so do Q_{diff} and Q_{H^*} [Eq. (35)]. W_{E^*} and Q_{E^*} do not. (b) We set $\chi = 0$ in Eq. (39), such that $\hat{H}_S$ commutes with $\hat{V}_{SUR}$ before and after the quench [Eqs. (31)]. The work dissipated during the system quench is plotted as a function of ϵ_B . The three curves coincide, as expected [Eq. (32)].

for work:

$$W_{\text{diff}} = \frac{\epsilon}{2} \tanh\left(\frac{\beta\epsilon}{2}\right) + \frac{\alpha}{2} \tanh\left(\frac{\beta\alpha}{2}\right) - \frac{2a_+ \sinh(\beta a_+) - 2\gamma \cosh(\beta a_+) + 2a_- \sinh(\beta a_-) + 2\gamma \cosh(\beta a_-)}{4 \cosh(\beta\epsilon/2) \cosh(\beta\alpha/2)}, \quad (\text{D19})$$

$$W_{H^*} = -\frac{1}{\beta} \left[\frac{e^{-\beta\epsilon/2} \ln(X_-) + e^{\beta\epsilon/2} \ln(X_+)}{2 \cosh(\beta\epsilon/2)} - \ln \left[2 \cosh\left(\frac{\beta\alpha}{2}\right) \right] \right] + \frac{\epsilon}{2} \tanh\left(\frac{\beta\epsilon}{2}\right), \quad (\text{D20})$$

and

$$W_{E^*} = \frac{\epsilon}{2} \tanh\left(\frac{\beta\epsilon}{2}\right) + \frac{\alpha}{2} \tanh\left(\frac{\beta\alpha}{2}\right) - \frac{1}{2 \cosh(\beta\epsilon/2)} \left[e^{-\beta\epsilon/2} \left(\frac{\partial_\beta X_-}{X_-} \right) + e^{\beta\epsilon/2} \left(\frac{\partial_\beta X_+}{X_+} \right) \right]. \quad (\text{D21})$$

Similarly, heat expressions follow from Eqs. (25) to (27):

$$Q_{\text{diff}} = \frac{1}{Z_{SUR}^B} \{ 2\gamma [e^{-\beta\gamma} \cosh(\beta\eta_+) - e^{\beta\gamma} \cosh(\beta\eta_-)] - 2\eta_+ e^{-\beta\gamma} \sinh(\beta\eta_+) - 2\eta_- e^{\beta\gamma} \sinh(\beta\eta_-) \} + \frac{2a_+ \sinh(\beta a_+) - 2\gamma \cosh(\beta a_+) + 2a_- \sinh(\beta a_-) + 2\gamma \cosh(\beta a_-)}{4 \cosh(\beta\epsilon/2) \cosh(\beta\alpha/2)}, \quad (\text{D22})$$

$$Q_{H^*} = \frac{1}{\beta} \left\{ \left[\frac{e^{-\beta\epsilon/2}}{2 \cosh(\beta\epsilon/2)} - \frac{X_-}{Z_{SUR}^B} \right] \ln(X_-) + \left[\frac{e^{\beta\epsilon/2}}{2 \cosh(\beta\epsilon/2)} - \frac{X_+}{Z_{SUR}^B} \right] \ln(X_+) \right\}, \quad (\text{D23})$$

and

$$Q_{E^*} = \left(\frac{e^{-\beta\epsilon/2}}{2X_- \cosh(\beta\epsilon/2)} - \frac{1}{Z_{SUR}^B} \right) \partial_\beta X_- + \left(\frac{e^{\beta\epsilon/2}}{2X_+ \cosh(\beta\epsilon/2)} - \frac{1}{Z_{SUR}^B} \right) \partial_\beta X_+. \quad (\text{D24})$$

The system's free energy changes by an amount

$$\Delta F_S = -\frac{1}{\beta} \ln \left(\frac{e^{-\beta\gamma} \cosh(\beta\eta_+) + e^{\beta\gamma} \cosh(\beta\eta_-)}{2 \cosh(\beta\epsilon/2) \cosh(\beta\alpha/2)} \right). \quad (\text{D25})$$

We compute the entropy change as we did for a system quench process (Appendix D 1), obtaining

$$\Delta\mathcal{S}_{\text{diff}} = \Delta\mathcal{S}_{E^*} = \frac{\beta\epsilon}{2} \tanh\left(\frac{\beta\epsilon}{2}\right) + \frac{\beta\alpha}{2} \tanh\left(\frac{\beta\alpha}{2}\right) - \frac{\beta}{Z_{\text{SUR}}^B} (\partial_\beta X_- + \partial_\beta X_+) + \ln\left[\frac{Z_{\text{SUR}}^B}{4 \cosh(\beta\epsilon/2) \cosh(\beta\alpha/2)}\right] \quad (\text{D26})$$

and

$$\Delta\mathcal{S}_{H^*} = \frac{\beta\epsilon}{2} \tanh\left(\frac{\beta\epsilon}{2}\right) - \frac{1}{Z_{\text{SUR}}^B} (X_- \ln X_- + X_+ \ln X_+) + \ln\left[2 \cosh\left(\frac{\beta\alpha}{2}\right)\right] + \ln\left[\frac{Z_{\text{SUR}}^B}{4 \cosh(\beta\epsilon/2) \cosh(\beta\alpha/2)}\right]. \quad (\text{D27})$$

3. LGT-type two-spin model

In Sec. VI, we introduced an LGT-type two-spin model [Eq. (39)]. One can generalize to this model Appendix D 1's expressions for work, heat, free energy, and entropy in the context of a system quench. One modifies the interaction term from $\gamma\sigma_S^z\sigma_R^z + \chi\sigma_S^x\sigma_R^x$ to $k(\mathbb{1}_{\text{SUR}} - \sigma_S^z\sigma_R^z) + \chi\sigma_S^x\sigma_R^x$ and takes the limit as $k \rightarrow \infty$. Equation (39) shows $\hat{H}_{\text{SUR}}$, in which the system term has a strength $\epsilon/2$. Consider switching ϵ instantaneously from $\epsilon_A = 0$ to ϵ_B [Fig. 1(a)]. α and χ remain fixed.

Figure 3(a) displays the dissipated work as a function of ϵ_B . The plot shows that W_{diff} and W_{H^*} obey the second law, while W_{E^*} does not. However, when $\chi = 0$, two behaviors stand out. First, all three dissipated-work quantities equal each other, in agreement with Eq. (32). Second, the quantities obey the second law.

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