Quantum heat distribution in thermal relaxation processes

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We analyze the heat exchange distribution of open quantum systems undergoing a thermal relaxation process with a time-dependent effective temperature. We show that such processes arise, for example, if the dynamics maximizes the entropy production. Using a two-point measurement scheme, we find an expression for the heat moment generating function that depends solely on the system's partition function and on the thermalization function (i.e., the law of cooling) describing the effective temperature. Applications include the relaxation of free bosonic and fermionic modes, for which closed-form expressions for the time-dependent heat distribution function are derived. Multiple free modes with arbitrary dispersion relations are also briefly discussed. In the semiclassical limit our formula agrees with previous results of the literature for the heat distribution of an optically trapped nanoscopic particle far from equilibrium.

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I. INTRODUCTION

In recent years significant results related to the nonequilibrium statistics of entropy production in open systems have been obtained [1–5]. A cornerstone of the field is the entropy fluctuation theorem (FT), which states that there is a special constraint in the asymmetry of the entropy production. In its integral form, the entropy FT reads $\langle e^{-\Delta_i S} \rangle = 1$, where $\Delta_i S$ is the entropy produced in some nonequilibrium thermodynamic process and the average is over all of the system's stochastic trajectories. From Jensen's inequality, the fluctuation theorem implies the Clausius inequality $\Delta_i S \geqslant 0$. Important particular cases of the FT are the Jarzynski equality [1], the heat exchange fluctuation theorem [5], and other less general forms [6,7], thus making the integral FT (and its detailed-balance versions [2]) a central result in stochastic thermodynamics [8–10].

Nonequilibrium thermodynamics was also applied to open quantum systems, including the analysis of time-dependent statistics of quantities such as heat and work [8,11–14], as well as quantum heat engines [15] and refrigerators [16,17]. Some exact nonequilibrium results have already been obtained experimentally [18] and a few analogous phenomena have been reported in the quantum information literature [19,20]. The extension of the FTs to open quantum systems is particularly subtle because of the role played in the theory by the measurement scheme [21–23]. For instance, there are different definitions of thermodynamic work depending on the methods used to account for the measurement effect, such as two-point-measurement (TPM) schemes and quantum jump methods [24–30], besides the fact that work is not a proper quantum observable [31]. It was only very recently that a path-integral formulation of quantum work [32] allowed its consistent definition in the presence of strong coupling.

There are also nonequilibrium situations, such as thermal relaxation processes, in which the quantity of interest is the

quantum heat [33]. In those cases, one can unambiguously argue that the thermodynamic work performed by or over the system is zero [22,32,34,35]. In such a situation, the heat Q exchanged with the reservoir can be identified by the energy variation between two projective measurements. In other words, if E_n (at t = 0) and E_m (at t > 0) are the energies obtained in two consecutive measurements, then the heat absorbed by the system is $Q = E_m - E_n$. The quantum heat Q is a stochastic quantity and obtaining a closed-form expression for its time-dependent distribution $P_t(Q)$ is not a trivial task. In fact, we are unaware of any previous exact result for the time-dependent heat distribution in quantum open systems. Furthermore, the current literature does not even offer a general qualitative understanding of nonequilibrium quantum heat distributions since they may depend on system specific properties [22]. Knowledge of the distribution $P_t(Q)$ is of both practical and conceptual importance in that it may help to address fundamental questions arising from nonequilibrium thermodynamics, as in the description of quantum engines [36,37], single-ion measurements [38–40], and the estimation of the probability of an apparent violation of the second law of thermodynamics in small systems [41,42].

In this paper we compute the distribution $P_t(Q)$ for a wide class of thermalization processes satisfying a rather general law of cooling. To be specific, we consider a TPM scheme (see Fig. 1) where the system is initially in thermal equilibrium with a reservoir of inverse temperature $\beta_1 = 1/T_1$. (Here the Boltzmann constant is set to unity $k_B = 1$.) At t = 0 a measurement is made yielding, say, an energy E_n , after which the system is placed in contact with a second reservoir with inverse temperature β_2 . At some later time t > 0 a second measurement is performed yielding an energy E_m . Repeating this procedure several times allows one to construct the heat probability distribution $P_t(Q)$, where $Q = E_m - E_n$. Here we are interested in quantum processes that map thermal states

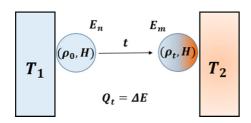


FIG. 1. A system (ρ_0, H) is initially prepared in thermal equilibrium with the first (blue) reservoir at temperature T_1 . At t=0, a projective energy measurement is performed, yielding the value E_n . Then the system is placed in contact with a second (red) reservoir at temperature T_2 . At time t>0, a second projective energy measurement is performed, yielding the value E_m . In this two-point measurement scheme, the heat exchanged between the system and the second reservoir is a time-dependent stochastic quantity $Q_t = E_m - E_n$ described by a nonequilibrium probability distribution $P_t(Q)$.

onto thermal states, characterized by a time-dependent effective temperature $\beta(t) = \phi_t(\beta_1, \beta_2)$, for some thermalization function ϕ_t that describes the specific law of cooling of the system in question. Note in particular that ϕ_t must obey the following relations: (i) $\phi_0(x, y) = x$, (ii) $\phi_\infty(x, y) = y$, and (iii) $\phi_t(x, x) = x$.

This general type of thermalization function has been found in several dynamics, such as in quasistatic processes [43–46], in Lindblad's dynamics of free bosonic [47] and fermionic modes [48], in general time evolution of glassy systems [49], in dynamical models for sheared foam [50], in the classical dynamics of optically trapped nanoparticles with experimental confirmation [51–53], and in the dynamics of some graphene models [54]. Furthermore, we will show below that under the assumption that the net heat transfer $\langle Q \rangle_t$ is fixed, the maximum entropy production implies that the system's density matrix $\rho(t)$ remains thermal for $t \ge 0$, with an effective temperature $\beta(t)$ as described above. This corroborates that such thermalization processes are indeed quite general in open quantum systems.

For such a broad class of systems that evolve through thermal states, we show that the nonequilibrium quantum heat statistics is, quite surprisingly, entirely determined by the equilibrium partition function $Z(\beta) = \sum_n e^{-\beta E_n}$. More precisely, we demonstrate that the time-dependent moment generating function (MGF) $M(s,t) = \langle e^{sQ} \rangle_t \equiv \int e^{sQ} P_t(Q) dQ$ of the quantum heat Q satisfies the remarkable identity

$$M(s,t) = \frac{Z(\beta_1 + s)}{Z(\beta_1)} \frac{Z(\phi_t(\beta_1 + s, \beta_2) - s)}{Z(\phi_t(\beta_1 + s, \beta_2))}.$$
 (1)

Two special cases of relation (1) are worth noting. First, setting s=0 yields M(0,t)=1, as required from the normalization condition $\int_{-\infty}^{\infty} P_t(Q)dQ=1$. Second, for $s=\Delta\beta=\beta_2-\beta_1$ we recover the integral fluctuation theorem [5]

$$M(\Delta \beta, t) = \langle e^{\Delta \beta Q} \rangle = 1,$$
 (2)

which follows immediately from the fact that $\phi_t(\beta_2, \beta_2) = \beta_2$ for all t. Furthermore, for systems that satisfy detailed balance, meaning that $P_t(n \to m) = e^{-\beta_2(E_m - E_n)}P_t(m \to n)$, where $P_t(n \to m)$ denotes the transition probability from state

 $|n\rangle$ to $|m\rangle$, one can show that the MGF possesses the symmetry

$$M(\Delta \beta - s, t) = M(s, t), \tag{3}$$

which is a direct manifestation of the detailed fluctuation theorem [55,56] $P_t(Q)/P_t(-Q) = e^{-\Delta\beta Q}$. Note, however, that the detailed FT, as expressed in Eq. (3), is a general property of systems obeying detailed balance, whereas Eq. (1) is a stronger result that relates nonequilibrium fluctuations with the equilibrium distribution for systems that obey a thermalization dynamics (not necessarily satisfying detailed balance). Relation (1) can thus be seen as a generalized fluctuation theorem that shows that the time-dependent heat distribution is fully encoded in the equilibrium partition function and in the underlying law of cooling, which accounts for the weak coupling with the reservoir. This result has important practical consequences, as it allows us to compute the nonequilibrium heat distribution $P_t(Q)$ for several systems of interest, as will be shown later.

II. THERMAL RELAXATION PROCESSES

We consider open quantum systems [57] whose time evolution is described by a linear dynamical map $\rho(t) = \Phi_t(\rho_0)$ with the semigroup property $\Phi_t(\Phi_s(\rho)) = \Phi_{t+s}(\rho)$ for $s, t \ge 0$. This implies in practice that for t > 0 the system is weakly coupled to the heat bath and that the evolution is memoryless (i.e., Markovian). The system starts at a thermal state with an inverse temperature β_1 : $\rho_0 = \rho_{\beta_1} \equiv e^{-\beta_1 H}/Z(\beta_1) = [Z(\beta_1)]^{-1} \sum_n e^{-\beta_1 E_n} |n\rangle \langle n|$. We analyze relaxation processes Φ_t with target state ρ_{β_2} , representing the second heat bath at inverse temperature β_2 , so that $\Phi_t(\rho_{\beta_2}) = \rho_{\beta_2}$ for all t. We will consider that the dynamics Φ_t is such that the thermal relaxation Φ_t satisfies a generic law of cooling of the type

$$\Phi_t(\rho_{\beta_1}) = \rho_{\phi_t(\beta_1, \beta_2)},\tag{4}$$

which maps an initial thermal state at inverse temperature β_1 onto a thermal state with an effective (time-dependent) inverse temperature $\beta(t) = \phi_t(\beta_1, \beta_2)$. It has been recently shown that thermalization is a rather general mechanism in quantum systems under a measurement process [58], and so the existence of an effective temperature applies to a broad class of open systems. In particular, we show below that if the dynamics Φ_t is such that the entropy production in the interval [0,t] is maximal, then Φ_t obeys the relation (4). Notice, however, that the property (4) comprises a wider class of dynamics in which the thermal relaxation is a particular case of interest. Other experimental setups satisfying (4) still benefit from the result (9) and they are left for future studies.

III. MAXIMUM-ENTROPY PRODUCTION

To establish (4) under the assumption of maximum-entropy production, first we consider that the system is in thermal equilibrium with a reservoir at temperature T_1 at t=0 and subsequently placed in contact with another heat bath at temperature T_2 , whose dissipative dynamics is represented by the map Φ_t . At time t>0, the nonequilibrium density matrix $\rho(t) = \Phi_t(\rho_0)$ has an associated von Neumann entropy variation $\Delta S = S[\rho] - S[\rho_0]$, where $S[\rho] = -\text{tr}(\rho \log \rho)$. One can write the entropy variation as $\Delta S = \Delta_i S + \Delta_e S$, where $\Delta_i S$ is

the entropy production (i.e., the irreversible component of the entropy change) and $\Delta_e S = \beta_2 \langle Q \rangle_t$ is the entropy exchanged with the environment (reservoir 2), corresponding to the reversible contribution to the entropy variation, with $\langle Q \rangle_t =$ $\langle H \rangle_t - \langle H \rangle_0 = \operatorname{tr}(\rho_t H) - \operatorname{tr}(\rho_0 H)$ the net heat absorbed by the system. According to Clausius inequality, the entropy production is positive $\Delta_i S \geqslant 0$. (We remark parenthetically that sharper lower and upper bounds for the irreversible entropy production have been recently established for open quantum systems [59,60].) Here we will require $\Delta_i S$ to be maximal for a constant heat exchange $\langle Q \rangle_t$. Thus, maximizing $\Delta_i S$ is equivalent to maximizing ΔS . This optimization problem may be written in the usual form $\delta(S_t - a_t \langle H \rangle_t + b_t \langle 1 \rangle) = 0$, where $\delta F(p)$ is understood as the functional derivative of F(p) with respect to the distribution p, and the Lagrangian multipliers a_t and b_t are needed to account for the constraint on the heat flux $\langle Q \rangle_t$ (and hence on $\langle H \rangle_t$ since $\langle H \rangle_0$ is fixed by the initial condition) and the normalization condition, respectively. Solving the optimization with these constraints results in a time-dependent thermal density matrix $\rho(t) = e^{-a_t H}/Z(a_t)$, where $Z(a_t) = \text{tr}[e^{-a_t H}]$, with $a_0 = \beta_1$ and $a_{\infty} = \beta_2$. From the constraint on $\langle H \rangle_t$, one can define a_t for any t > 0 from the formula $\langle H \rangle_t = -\partial \ln Z(a_t)/\partial a_t$. Solving for a_t yields the law of cooling $a_t = \phi_t(\beta_1, \beta_2)$. Note that this is equivalent to the property defined in Eq. (4), which states that the dynamical map Φ_t evolves initial thermal states onto thermal states for all t > 0.

It is perhaps worth pointing out that the above argument remains valid if instead of the von Neumann entropy one uses the Wigner entropy production, yielding the same law of cooling as (4), with the advantage that the entropy flux stays finite for $T \to 0$ [61] (see Supplemental Material also [62]).

IV. HEAT DISTRIBUTION

Starting from the generic thermalization dynamics given in Eq. (4), we now prove that the heat distribution obeys the fluctuation relation given in Eq. (1). We recall that in the TPM scheme, the system starts at thermal equilibrium with the first reservoir at temperature T_1 , and at t=0 an energy measurement is performed yielding the value E_n with probability $p_n = e^{-\beta_1 E_n}/Z(\beta_1)$, thus projecting the system onto the energy eigenstate $|n\rangle\langle n|$. Subsequently, the system is placed in thermal contact with a second reservoir at temperature T_2 , represented by the map Φ_t with the cooling property (4). A second energy measurement is then performed on the system at some time t>0, now with the time propagated density matrix $\Phi_t(|n\rangle\langle n|)$, yielding the value E_m and projecting the system onto the energy eigenstate $|m\rangle\langle m|$. The moment generating function of the exchanged heat $Q=E_m-E_n$ is defined as

$$\langle e^{sQ} \rangle = \sum_{n,m} e^{s(E_m - E_n)} p_n \langle m | \Phi_t(|n\rangle \langle n|) | m \rangle.$$
 (5)

Using the linearity of Φ_t and combining the terms in p_n and e^{-sE_n} , we can rewrite the sum over n in Eq. (5) in terms of a new thermal state that depends on the real parameter s (provided $s + \beta_1 \ge 0$), thus obtaining

$$\langle e^{sQ} \rangle = \frac{Z(\beta_1 + s)}{Z(\beta_1)} \sum_{m} e^{sE_m} \langle m | \Phi_t(\rho_{\beta_1 + s}) | m \rangle \tag{6}$$

(see details in Supplemental Material Ref. [62]). Finally, we apply the property (4) to write $\Phi_t(\rho_{\beta_1+s}) = \rho_{\phi_t(\beta_1+s,\beta_2)} = e^{-\phi_t(\beta_1+s,\beta_2)H}/Z(\phi_t(\beta_1+s,\beta_2))$, which inserted into (6) and summing over m results in Eq. (1). Next we will make use of the MGF (1) to compute explicitly the heat distribution $P_t(Q)$ for a variety of systems.

V. BOSONIC MODES

Here we apply (1) to a system composed of a single bosonic mode coupled to a thermal bath. The system is described by the Hamiltonian of the harmonic oscillator $H = \hbar \omega (a^{\dagger} a + 1/2)$ and its partition function is $Z(\beta) = (1/2) \operatorname{csch}(\beta \hbar \omega/2)$. In this representation, the system satisfies a Lindblad equation [61]

$$\partial_t \rho = \frac{-i}{\hbar} [H, \rho] + D_i(\rho) \tag{7}$$

with the dissipator

$$D_{i}(\rho) = \gamma(\overline{n}_{i} + 1) \left[a\rho a^{\dagger} - \frac{1}{2} \{ a^{\dagger} a, \rho \} \right]$$
$$+ \gamma \overline{n}_{i} \left[a^{\dagger} \rho a - \frac{1}{2} \{ a^{\dagger} a, \rho \} \right]$$
(8)

and an average number of excitations $\bar{n}_i = [\exp(\hbar\omega/k_BT_i) - 1]^{-1}$, i = 1, 2, that depends on the temperature of the reservoir coupled to the system. One can verify, using the operator formalism [47,63], that the dynamics (7) does indeed satisfy a law of cooling of the type shown in Eq. (4). This result can be obtained more directly using the Wigner function representation and its associated stochastic parametrization. More specifically, one can show (see Supplemental Material [62]) that the dynamics given by (7) and (8) propagates any thermal distribution with inverse temperature β_1 to another thermal distribution with an effective time-dependent temperature defined by $\bar{n}_t = (\bar{n}_1 - \bar{n}_2)e^{-\gamma t} + \bar{n}_2$, where $\bar{n}_t = [\exp(\hbar\omega/k_BT_t) - 1]^{-1}$, which can be solved to yield $\beta(t) \equiv 1/k_BT_t = \phi_t(\beta_1, \beta_2)$.

It is worth mentioning that in the semiclassical limit, where $\hbar\omega(\bar{n}_i+1/2) \to k_B T_i$, one recovers Newton's law of cooling $T_t = T_2 + (T_1 - T_2)e^{-\gamma t}$. Note that although the effective temperature T_t evolves from T_1 (at t=0) and reaches T_2 for $t\to\infty$ in both the quantum and the classical cases, the transient behaviors differ considerably, as depicted in Fig. 2.

Having found that the system (7) satisfies a law of cooling as in Eq. (4), a remarkably elegant expression for the heat MGF M(s,t) can now be obtained by using Eq. (1) with $Z(\beta) = (1/2)\operatorname{csch}(\beta\hbar\omega/2)$. We find

$$M(s,t) = \left[1 - \frac{\sinh\left(\frac{\hbar}{2}\omega s\right)\sinh\left[\frac{\hbar}{2}\omega(s - \Delta\beta)\right]}{\sinh\left(\frac{\hbar}{2}\omega\beta_1\right)\sinh\left(\frac{\hbar}{2}\omega\beta_2\right)}(1 - e^{-\gamma t})\right]^{-1},$$
(9)

where $\Delta\beta = \beta_2 - \beta_1$. This equation reproduces, after some algebra, a recent result reported in Ref. [64]. As a check, note that M(0,t)=1, whereas for $s=\Delta\beta$ we indeed obtain (2). Furthermore, Eq. (9) displays the symmetry (3), as expected, since the system is known to satisfy detailed balance.

Remarkably, we are also able to find (see Supplemental Material [62]) the nonequilibrium probability distribution of the exchanged heat, $Q = E_m - E_n = \hbar\omega(m-n) = \hbar\omega k$, a

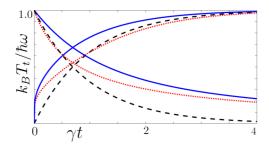


FIG. 2. Different laws of cooling (effective temperatures) of the bosonic mode (solid blue line) and the fermionic mode (dotted red line) and the classical Newton law of cooling (dashed black line) as a function of time. The descending lines represent cooling from $k_BT_1/\hbar\omega=1$ to $k_BT_2/\hbar\omega=10^{-3}$. The rising lines represent the heating process from $k_BT_1/\hbar\omega=10^{-3}$ and $k_BT_2/\hbar\omega=1$. Note that the bosonic line (blue) decays slower in the cooling process and rises faster in heating when compared to its semiclassical limit (dashed). The fermionic starts by heating faster, but then becomes slower than the semiclassical limit. In the cooling process, the fermionic mode starts close to the classical case, but eventually slows down.

task that was deemed not possible in Ref. [64]. We obtain

$$P_t(Q = \hbar \omega k) = \frac{2\nu_t \mu_t}{\mu_t^2 - 1} \exp\left(-|k| \ln \mu_t - k \frac{\hbar \omega \Delta \beta}{2}\right)$$
 (10)

for any integer $k = \{\dots, -1, 0, +1, \dots\}$, with time-dependent parameters (v_t, μ_t) given by $v_t = 2 \sinh(\hbar \omega \beta_1/2) \sinh(\hbar \omega \beta_2/2)/(1 - e^{-\gamma t})$, $\mu_t = \Omega_t + \sqrt{\Omega_t^2 - 1}$, and $\Omega_t = v_t + \cosh(\hbar \omega \Delta \beta/2)$. Note in particular that the detailed FT holds: $P_t(Q = \hbar \omega k)/P_t(Q = -\hbar \omega k) = e^{-Q\Delta\beta}$. Notably, we may also use (10) to find the probability of a heat flow from lower to higher temperature. To see this, suppose that $T_2 > T_1$. In this case, one expects a positive heat (Q > 0) absorbed by the system. However, since Q is a random variable, there is a probability of a reverse heat flow $(Q \le 0)$ given by

$$P_t(Q \le 0) = \frac{2\nu_t \mu_t}{\mu_t^2 - 1} \frac{1}{1 - \mu_t^{-1} e^{\hbar \omega \Delta \beta/2}}.$$
 (11)

This apparent violation of the second law of thermodynamics is indeed observed in small systems [65]. Before leaving this section, we remark that a perturbation in the Hamiltonian which is linear in a and a^{\dagger} , such as in the case of a single mode cavity pumped by a radiation field, does not change the heat MGF (9) since the pump only shifts the spectrum E_n by a constant, which keeps the energy variations ($\Delta E = E_m - E_n$) invariant (see Supplemental Material [62]). Thus, the relation (9) can in principle be tested in optical cavities far from equilibrium.

VI. UNDERDAMPED CLASSICAL OSCILLATORS

The semiclassical limit of Eq. (9) is obtained by taking $\hbar\omega\beta_i \to 0$ and $\hbar\omega s \to 0$. We find

$$M(s,t) = \left(1 - \frac{s(s - \Delta\beta)}{\beta_1 \beta_2} (1 - e^{-\gamma t})\right)^{-1}.$$
 (12)

Note in particular that in the case of f/2 independent harmonic oscillators we have $M_{f/2}(s,t) = [M(s,t)]^{f/2}$, which,

combined with (12), reproduces the result for the heat distribution of f/2 classical nanoscopic particles optically trapped in the highly underdamped limit [51–53].

VII. FERMIONIC MODE

Consider a free fermionic mode with Hamiltonian $H=\hbar\omega a^{\dagger}a$ and the usual anticommutating relation $\{a^{\dagger},a\}=1$. The system has two eigenstates $\{|0\rangle,|1\rangle\}$. Given an initial state $v=(1-\overline{n},\overline{n})$, suppose its dynamics is Markovian and satisfies detailed balance. Then, starting at an initial temperature T_1 , the evolution of the state is given by the same law of cooling found in the bosonic case, namely, $\overline{n}_t=\overline{n}_2+(\overline{n}_1-\overline{n}_2)e^{-\gamma t}$, but where now n_i is the fermionic occupation number $\overline{n}_i=[\exp(\beta_i\hbar\omega)+1]^{-1}$, i=1,2, for some damping constant $\gamma>0$, obtained from the unique free parameter in the dynamics (see Supplemental Material [62]). The fermionic law of cooling is also depicted in Fig. 2. In this case, the heat exchange MGF reads

$$M(s,t) = 1 + \frac{\sinh(\hbar\omega s/2)\sinh[\hbar\omega(s-\Delta\beta)/2]}{\cosh(\hbar\omega\beta_1/2)\cosh(\hbar\omega\beta_2/2)}(1 - e^{-\gamma t}).$$
(13)

Note the striking similarities between this result and that for the bosonic case shown in Eq. (9). In particular, Eq. (13) has the expected behavior for s = 0 and $s = \Delta \beta$ and satisfies (3) as well. The heat probability distribution is found straightforwardly from (13) to be

$$P_t(Q = \pm \hbar \omega) = \frac{(1 - e^{-\gamma t})e^{\mp \hbar \omega \Delta \beta/2}}{4\cosh(\hbar \omega \beta_1/2)\cosh(\hbar \omega \beta_2/2)}, \quad (14)$$

with $P_t(Q=0) = 1 - [P_t(\hbar\omega) + P_t(-\hbar\omega)]$.

VIII. CONCLUSION AND PERSPECTIVES

We have shown that a thermal relaxation process that maximizes the entropy production (for fixed heat exchange) satisfies a law of cooling of the form shown in Eq. (4). We proved that any system relaxing in this way has a heat moment generating function given by Eq. (1), which depends only on the equilibrium partition function $Z(\beta)$ and the cooling function $\phi_t(\beta_1, \beta_2)$. We used this general result to find the heat distribution of a number of experimentally relevant systems, such as a single bosonic mode, the semiclassic limit of optically trapped nanoparticles, and a single fermionic mode. We emphasize that the maximum-entropy production principle may also be useful in deriving approximate cooling laws for a large class of systems with tight bounds on the entropy production [59], where a nonequilibrium effective temperature can be defined. As a closing remark, we point out that the framework derived here can be easily generalized to include the study of quantum heat statistics of a system with multiple independent modes, such as Bose-Einstein condensates and the relaxation dynamics of spin chains. The development of this interesting perspective is left for future work.

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