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Stochastic thermodynamics of a finite quantum system coupled to a heat bath

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Abstract: We consider a situation where an *N*-level system (NLS) is coupled to a heat bath without being necessarily thermalized. For this situation, we derive general Jarzynski-type equations and conclude that heat and entropy is flowing from the hot bath to the cold NLS and, vice versa, from the hot NLS to the cold bath. The Clausius relation between increase of entropy and transfer of heat divided by a suitable temperature assumes the form of two inequalities which have already been considered in the literature. Our approach is illustrated by an analytical example.

Keywords: Clausius inequalities; Jarzynski equations; second law.

1 Introduction

The study of nonequilibrium thermodynamics of systems in contact with a thermal reservoir ("heat bath") of different temperatures has a long history. As an example of the approach via a Master equation and its weak coupling limit, we mention the work of Lebowitz and Spohn [1], which actually considers a finite number of reservoirs. During the last decades, new methods have been devised, in particular, the approach via fluctuation theorems [2]. The famous Jarzynski equation represents one of the rare exact results of nonequilibrium statistical mechanics. It is a statement about the expectation value of the exponential of the work $\langle e^{-\beta w} \rangle$ performed on a system initially in thermal equilibrium with inverse temperature β , but possibly far from equilibrium after the work process. This equation was first formulated for classical systems [3] and subsequently

proved for quantum systems [4-6]. Extensions for systems that are initially in local thermal equilibrium [5], microcanonical ensembles [7], and grand-canonical ensembles [8-14] have been published. The literature on the Jarzynski equation and its applications is rich; a concise review is given in [14], focusing on the connection with other fluctuation theorems. The most common approach to the quantum Jarzynski equation is to consider sequential measurements. This approach is also followed in the present work. The general framework for such an approach was outlined in [15] and [16]. It is *per se* neither quantum mechanical nor classical and will be referred to as "stochastic thermodynamics" in the present work. At the end of Appendix C, we sketch realizations of the general framework in quantum mechanics and classical mechanics.

Interestingly, one can derive from the Jarzynski equation certain inequalities that resemble the second law, see, e.g., [14]. However, a closer inspection shows that these inequalities are not exactly statements about the non-decrease of entropy. But the entropy balance is not the problem: the total von Neumann entropy is constant during unitary time evolution and non-decreasing during projective measurements, see [17] or Theorem 11.9 in [18]. The problem is rather that in the quantum case, the entropy balance is not sufficient to cover all aspects of the second law.

To explain the latter, consider classical thermodynamics where there are several equivalent formulations of the second law. For example, from the non-decrease in total entropy, it can be deduced that heat (and entropy) always flows from the hotter to the colder body. The elementary argument goes as follows: If the hotter body with inverse temperature β transfers the infinitesimal heat δQ (of whatever sign) to the colder body with inverse temperature $\beta_0 > \beta$, then its entropy decrease will be $dS_1 = \beta \delta Q$, according to the Clausius equality. On the other hand, the colder body receives the heat δQ and its entropy increases by $dS_2 = \beta_0 \delta Q$. The total entropy increase will be $dS = dS_2 - dS_1 = (\beta_0 - \beta)\delta Q$. Since $(\beta_0 - \beta) > 0$, we obtain $dS \ge 0 \Leftrightarrow \delta Q \ge 0$.

In the quantum case, this elementary argument breaks down. Between the two sequential measurements, the transferred heat ΔQ and entropy ΔS can no longer be considered as infinitesimal and the Clausius equality has to be

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replaced by two inequalities. Moreover, the energy increase of the first system is not exactly equal to the energy decrease of the second system. This holds only approximately if the interaction Hamiltonian can be neglected, which will not be the case for small ΔQ . (Strictly speaking, the latter objection already applies to the classical case.)

We will try here to modify the classical argument for the "correct" heat flow for quantum mechanics. To this end, we will adopt another approach to the problem of the direction of the heat flow that focuses on the *N*-level quantum system and describes the influence of the heat bath solely in terms of a transition matrix T. T is only a (left) stochastic matrix and can no longer be assumed to be bi-stochastic (in the strict or modified sense) and hence, the usual assumptions leading to a Jarzynski-type equation, see [15], are no longer satisfied. But it is possible to derive a more general J-equation that is only based on (left) stochasticity of T. Thus, we can find arguments for the "correct" flow of heat and entropy that only rely on the assumption that *T* leaves invariant some Gibbs state with inverse temperature β_0 , see Section 2. β_0 is interpreted as the inverse temperature of the heat bath. In this sense, we derive the second law of thermodynamics from a form of the zeroth law. For this derivation, we combine known results that appear in various places in the literature, see [19-23], but are sometimes only proved under assumptions that are stronger than those we will assume in the present work. We will present the relationship of these references to our results in more detail in Section 4.

The structure of the paper is as follows. The general definitions and main results on the heat flow between the system and the heat bath are given in Section 2. These results are based on a Jarzynski-type equation (19), which is proved in a more general setting in Appendix C. Here, we also comment on the possibility to relax the usual assumption of an initial product state. Close to the equilibrium point, the entropy increase ΔS and the absorbed heat over temperature $\beta \Delta Q$ have a common tangent, see Figure 1, with a positive slope, as proved in Appendix B. The analogous result on the entropy flow is formulated in Section 3. It depends on two "Clausius inequalities", see Eq. (67), the second one of which again follows from the Jarzynski-type equation. The bi-stochastic limit is shortly considered in Section 4. The next Section 5 contains an analytically solvable example. We close with a summary and outlook in Section 6.

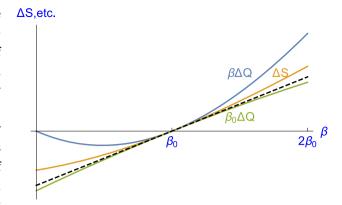


Figure 1: Typical plot of the two "Clausius heat terms" $\beta_0 \Delta Q$, $\beta \Delta Q$, and the "entropy increase" ΔS as functions of the inverse temperature β of the NLS calculated for a randomly chosen transition matrix T and N=4. Note that $\beta_0 \Delta Q \leq \Delta S \leq \beta \Delta Q$ holds in accordance with (67). The inverse temperature of the heat bath is β_0 , where all three functions vanish and have a common tangent (dashed black line) with the slope a according to (56).

2 Main results on heat flow

We consider an N-level system (NLS) described by a finite index set \mathcal{N} , energies E_n , and degeneracies d_n for $n \in \mathcal{N}$. The NLS is assumed to be initially in a Gibbs state with probabilities

$$p_n = \frac{d_n}{Z} \exp\left(-\beta E_n\right),\tag{1}$$

where the partition function Z is defined by

$$Z = \sum_{n} d_n \, \exp\left(-\beta \, E_n\right),\tag{2}$$

and $\beta = \frac{1}{\tau}$ is the inverse temperature of the NLS. After an interaction with a heat bath a subsequent measurement of energy finds the NLS in the level $m \in \mathcal{N}$ with probability

$$q_m = \sum_n P(m \leftarrow n) \, p_n \equiv \sum_n T_{\text{mn}} \, p_n. \tag{3}$$

Here, the "transition matrix" T is an $N \times N$ (left) stochastic matrix, i.e., satisfying

$$T_{\rm mn} \ge 0 \quad \text{for all } m, n \in \mathcal{N},$$
 (4)

$$\sum_{m} T_{mn} = 1 \quad \text{for all } n \in \mathcal{N}. \tag{5}$$

The entries of T will be sometimes written as conditional probabilities $T_{mn}=P(m\leftarrow n)$ with self-explaining notation. We do not make any assumptions concerning thermalization and hence, the final probabilities q_m will, in general, not be of Gibbs type.

The usual Jarzynski equation is based on the property of T being a bi-stochastic matrix, i.e., additionally satisfying, in the non-degenerate case of $d_n \equiv 1$,

$$\sum_{n} T_{mn} = 1 \quad \text{for all } m \in \mathcal{N}, \tag{6}$$

or, in the general case,

$$\sum_{n} T_{mn} d_n = d_m \quad \text{for all } m \in \mathcal{N}, \tag{7}$$

see Eq. (25) in [15]. This property holds if the system is closed and only subject to external forces performing work upon the system. But bi-stochasticity is no longer guaranteed for systems coupled to other ones (heat baths). However, if this is the case and if no external forces are applied, we may relax the (modified) bi-stochasticity of T to the following:

Assumption 1. There exists a Gibbs state with probabilities

$$p_n^{(0)} = \frac{d_n}{Z_0} \exp(-\beta_0 E_n),$$
 (8)

and

$$Z_0 = \sum_{n} d_n \, \exp(-\beta_0 \, E_n) \,, \tag{9}$$

that is left fixed by *T*, i.e.,

$$\sum_{n} T_{mn} p_n^{(0)} = p_m^{(0)} \quad \text{for all } m \in \mathcal{N}.$$
 (10)

In this case, the transition matrix T, satisfying (4), (5) and (10), will be called a "Gibbs matrix" with temperature $\tau_0 = \frac{1}{6}$. We will also refer to τ_0 as the "temperature of the heat bath".

Recall that every (left) stochastic matrix T has an eigenvector $p^{(0)}$ with non-negative entries corresponding to the eigenvalue 1, although $p^{(0)}$ is generally not unique. If the entries $p_n^{(0)}$ are different and positive, one can always define suitable energies $E_n := -\log p_n^{(0)}$ such that (8) holds with $\beta_0 = 1$ and $d_n \equiv 1$. This has been used to generate numerical examples of Gibbs matrices, see Figures 1 and 2. Mathematically, T being bi-stochastic is a special case of being a Gibbs matrix, since (6) follows from (10) for $\beta_0 = 0$ and $d_n = 1$ for all $n \in \mathcal{N}$. However, according to the above remarks, being a Gibbs matrix should rather be considered as a property of T relative to a given family of energies E_n , not as a property of T alone.

Physically, the property (10) appears plausible if *T* represents the transition matrix due to the interaction with a heat bath of temperature τ_0 . If the NLS already has the same temperature τ_0 , its state should not change. This is not trivial since, in general, the Gibbs state of the combined

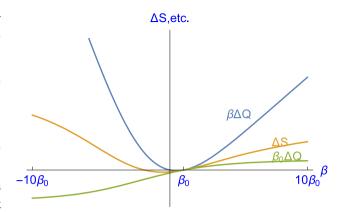


Figure 2: The same plot as in Figure 1 but for the extended range of inverse temperatures $-10\beta_0 \le \beta \le 10\beta_0$ of the NLS. Note that also in this extended range $\beta_0 \Delta Q \leq \Delta S \leq \beta \Delta Q$ holds in accordance with (67). For negative temperatures, these "Clausius inequalities" are less restrictive since here $\beta_0 \Delta Q$ and $\beta \Delta Q$ have different signs. ΔS has a second zero for negative inverse temperatures that, in contrast to the first zero at $\beta = \beta_0$, does not correspond to a fixed point of the transition matrix T. For $\beta \to \pm \infty$, the Gibbs state probability $p(\beta)$ is concentrated on the level with the lowest/highest energy, respectively, and hence $\beta_0 \Delta Q$ as well as ΔS approach constant values. Therefore, $\beta \Delta Q$ is asymptotically linear at these limits.

system, NLS plus heat bath, with temperature au_0 does not commute with the interaction Hamiltonian. However, it can be shown that (10) holds exactly for some analytically solvable examples [24], and in other cases, the real situation can be expected to be represented by (10) to an excellent approximation.

Next, we will recall some probabilistic framework concepts for the Jarzynski-type equation, see [15]. Let $\mathcal{N} \times \mathcal{N}$ be the set of "elementary events" such that one event $(m,n) \in \mathcal{N} \times \mathcal{N}$ represents the outcome of a sequential energy measurement at the NLS in the sense that the initial measurement yields the result E_n , and, after the interaction with the heat bath, the final measurement yields E_m . The probability function

$$P: \mathcal{N} \times \mathcal{N} \to [0, 1] \tag{11}$$

defined for elementary events is given by

$$P(m,n) = P(m \leftarrow n) p_n = T_{mn} \frac{d_n}{Z} \exp(-\beta E_n).$$
 (12)

Analogously to the case of the ordinary Jarzynski equation, we consider random variables $Y: \mathcal{N} \times \mathcal{N} \to \mathbb{R}$ and their expectation value denoted by

$$\langle Y \rangle := \sum_{mn} P(m,n) Y(m,n) = \sum_{mn} T_{mn} p_n Y(m,n).$$
 (13)

An example is

$$\Delta Q: \mathcal{N} \times \mathcal{N} \to \mathbb{R} \tag{14}$$

defined by

$$\Delta Q(m,n) := E_m - E_n. \tag{15}$$

This can be interpreted as the "heat" transferred to the NLS during the interaction with the heat bath since we have assumed that no external forces are active that could perform work on the NLS.

Another example is the random variable "entropy increase"

$$\Delta S: \mathcal{N} \times \mathcal{N} \to \mathbb{R} \tag{16}$$

defined by

$$\Delta S(m,n) := \log \frac{p_n}{d_n} - \log \frac{q_m}{d_m}. \tag{17}$$

Its expectation value agrees with the familiar expression for entropy decrease, as will be shown in Section 3, see Eqs. (35)–(37).

Sometimes, instead of (13), we will also use the sloppy notation $\langle Y(m, n) \rangle$ for the expectation value.

Then we can state the following Jarzynski-type equation that follows from the general "J-equation" considered in Appendix C.

Theorem 1. If T is a Gibbs matrix with inverse temperature β_0 and \widetilde{p} an arbitrary probability distribution, hence satisfying

$$\sum_{n \in \mathcal{N}} \widetilde{p}_n = 1,\tag{18}$$

then, under the preceding conditions, the following holds:

$$\left\langle \frac{p_n^{(0)} \widetilde{p}_m}{p_m^{(0)} p_n} \right\rangle = 1.$$
 (19)

For the proof see Appendix C, where (19) is obtained as a special case.

The Jarzynski-type equation (19) is more of a template that can be used to generate further equations by choosing a special form of the general probability distribution \widetilde{p} . As a particular choice, we will consider $\tilde{p} = p$. This yields

$$\left\langle \frac{p_n^{(0)} p_m}{p_m^{(0)} p_m} \right\rangle = 1,$$
 (20)

and further, using

$$\frac{p_m}{p_n} = \frac{d_m}{d_n} \exp\left(-\beta \left(E_m - E_n\right)\right),\tag{21}$$

$$\frac{p_n^{(0)}}{p_{n}^{(0)}} = \frac{d_n}{d_m} \exp\left(-\beta_0 \left(E_n - E_m\right)\right),\tag{22}$$

and (15), the following equation:

$$\left\langle e^{-(\beta-\beta_0)\Delta Q} \right\rangle = 1.$$
 (23)

This equation was also derived in [19] under stronger assumptions. As pointed out in [19], Eq. (23) implies that the probability of events where heat flows in the "wrong" direction, i.e., where $(\beta - \beta_0) \Delta Q < 0$, must be exponentially suppressed. The reason is that in the case of a Jarzynski-type equation of the form $\langle e^X \rangle = 1$ the contributions to the expectation value from large positive values of X must be counterbalanced by a large number of contributions from negative values of *X* in order to maintain the expectation value at 1.

As for the original Jarzynski equation, we may derive an inequality by invoking Jensen's inequality (JI). Note that $x \mapsto -\log x$ is a convex function. Hence

$$0 = -\log 1 \stackrel{(23)}{=} -\log \langle \exp(-(\beta - \beta_0) \Delta Q) \rangle$$
 (24)

$$\stackrel{(II)}{\leq} \langle -\log \exp(-(\beta - \beta_0) \Delta Q) \rangle = (\beta - \beta_0) \langle \Delta Q \rangle. \quad (25)$$

Thus, we have proven:

Theorem 2.

$$(\beta - \beta_0) \langle \Delta Q \rangle \ge 0. \tag{26}$$

If the temperature au of the NLS is lower than the temperature τ_0 of the heat bath, then $\beta - \beta_0 \ge 0$ and hence, by means of (26), $\langle \Delta Q \rangle \ge 0$. It means that in this case the expectation value of the heat flowing into the NLS will be positive, and vice versa. In other words, heat will flow from the hotter body to the colder one, analogously to the result in classical thermodynamics, see Section 1.

3 Clausius inequalities

We adopt the notation of Section 2 but for the next steps will not need Assumption 1. Further define (sometimes skipping the expectation brackets $\langle ... \rangle$ if no misunderstanding can occur):

$$E(p) := \sum p_n E_n, \tag{27}$$

$$E_2(p) := \sum p_n E_n^2, (28)$$

$$E(q) := \sum_{n=0}^{\infty} q_n E_n, \tag{29}$$

$$\Delta E := E(q) - E(p), \tag{30}$$

$$S(p) := -\sum_{n} p_n \log \frac{p_n}{d_n}, \tag{31}$$

$$S(q) := -\sum_{n} q_n \log \frac{q_n}{d_n},\tag{32}$$

$$\Delta S := S(q) - S(p). \tag{33}$$

Note that (1) implies the familiar identity

$$S(p) \stackrel{(1)}{=} \sum_{n} p_n (\beta E_n + \log Z) \stackrel{(27)}{=} \beta E(p) + \log Z.$$
 (34)

To show the consistency of (33) with the definition (17), we calculate the expectation value of the corresponding random variable

$$\langle \Delta S \rangle \stackrel{\text{(13)}}{=} \sum_{mn} T_{mn} \, p_n \, \left(\log \frac{p_n}{d_n} - \log \frac{q_m}{d_m} \right) \tag{35}$$

$$\stackrel{\text{(3.5)}}{=} \sum_{n} p_{n} \log \frac{p_{n}}{d_{n}} - \sum_{m} q_{m} \log \frac{q_{m}}{d_{m}}$$

$$\stackrel{\text{(31.32)}}{=} S(q) - S(p),$$
(36)

$$\stackrel{(31,32)}{=} S(q) - S(p), \tag{37}$$

which agrees with (33).

Then, we can show the following:

Theorem 3. Under the preceding conditions, the "first Clausius inequality"

$$\beta \langle \Delta E \rangle \ge \langle \Delta S \rangle \tag{38}$$

holds.

This inequality has also be obtained in [20] by considering two systems with weak interaction and using the fact that the Gibbs state minimizes the free energy. This statement, in turn, can also be proven by the Gibbs inequality used below.

Proof of Theorem 3. For any two probability distributions $p, q: \mathcal{N} \to [0, 1]$ there holds the Gibbs inequality or nonnegativity of the KL-divergence

$$S(q||p) := \sum_{n} q_n \log \frac{q_n}{p_n} \ge 0,$$
 (39)

see, e.g., Theorem 11.1 in [18]. From this, we obtain

$$-S(q) \stackrel{(32)}{=} \sum_{n} q_n \log \frac{q_n}{d_n} \tag{40}$$

$$\geq \sum_{n} q_n \log \frac{p_n}{d_n} = -\beta E(q) - \log Z, \tag{41}$$

and further

$$\beta \Delta E \stackrel{(30)}{=} \beta \left(E(q) - E(p) \right) \tag{42}$$

$$\stackrel{(34)}{=} \beta E(q) - S(p) + \log Z \tag{43}$$

$${\stackrel{(41)}{\geq}} S(q) - S(p) \stackrel{(33)}{=} \Delta S, \tag{44}$$

which concludes the Proof of Theorem 3.

Interestingly, the first Clausius inequality can be sharpened to a Clausius equality in the weak coupling limit.

Proposition 1. *If the transition matrix T is of the form*

$$T = 1 + \varepsilon t + O(\varepsilon^2), \qquad (45)$$

where t denotes some $N \times N$ -matrix with necessarily vanishing column sums, then

$$\Delta S = \beta \Delta E + O(\varepsilon^2). \tag{46}$$

The proof can be found in Appendix A.

Next, we assume the situation of a "heat process" as in Section 2 together with Assumption 1 and hence, can interpret the energy difference $\langle \Delta E \rangle$ as the heat $\langle \Delta Q \rangle$ transferred to the NLS. We consider both sides of (38), $\beta \langle \Delta O \rangle$ and $\langle \Delta S \rangle$, as functions of the inverse temperature β . Both functions vanish at the inverse temperature β_0 of the heat bath and, due to (38), must have a common tangent at $\beta = \beta_0$, see Figure 1. We will calculate its slope a using the intermediate results

$$\frac{\partial p_n}{\partial \beta} \stackrel{(1,2)}{=} p_n \left(E(p) - E_n \right) \tag{47}$$

$$\frac{\partial E(p)}{\partial \beta} \stackrel{(27,47)}{=} \sum p_n \left(E(p) - E_n \right) E_n \tag{48}$$

$$\stackrel{(28)}{=} E(p)^2 - E_2(p) \tag{49}$$

$$\frac{\partial q_n}{\partial \beta} \stackrel{(3)}{=} \sum_m T_{nm} \frac{\partial p_m}{\partial \beta} \tag{50}$$

$$\stackrel{(47)}{=} \sum_{m} T_{nm} \, p_m \, \left(E(p) - E_m \right) \tag{51}$$

$$=q_n E(p) - \sum_m T_{nm} p_m E_m$$
 (52)

$$\frac{\partial E(q)}{\partial \beta} \stackrel{(29)}{=} \sum_{n} \frac{\partial q_n}{\partial \beta} E_n \tag{53}$$

$$\stackrel{(50)}{=} \sum_{n} \left(q_n E(p) - \sum_{m} T_{nm} p_m E_m \right) E_n \tag{54}$$

$$= E(q)E(p) - \sum_{mm} T_{nm} \, p_m \, E_m \, E_n. \tag{55}$$

This yields

$$a := \frac{\partial}{\partial \beta} \beta \langle \Delta Q \rangle \bigg|_{\beta = \beta_0} \tag{56}$$

$$=\underbrace{\langle \Delta Q \rangle|_{\beta=\beta_0}}_{=0} + \beta_0 \frac{\partial}{\partial \beta} \langle \Delta Q \rangle \bigg|_{\beta=\beta_0}$$
 (57)

$$\stackrel{(30,48,53)}{=} \beta_0 \left(E(q)E(p) - \sum_{nm} T_{nm} \, p_m \, E_m \, E_n - E(p)^2 + E_2(p) \Big|_{\beta = \beta_0} \right)$$
(58)

$$= \beta_0 \left(E_2(p^{(0)}) - \sum_{nm} T_{nm} \, p_m^{(0)} \, E_m \, E_n \right) \tag{59}$$

$$= \beta_0 \left(\sum_{nm} T_{nm} \, p_m^{(0)} \, E_m \, (E_m - E_n) \right), \tag{60}$$

using Eq. (5) in (60). According to Theorem 1, it is clear that the slope of the tangent cannot be negative, $a \ge 0$. Nevertheless, this will be checked independently, see Appendix B.

The linear part of the Taylor series of $\beta \langle \Delta Q \rangle$ w.r.t. $(\beta - \beta_0)$ can be used to re-write $\langle \Delta Q \rangle$ as a function of the dimensionless temperature $\tau = \frac{1}{6}$ such that the zero of $\langle \Delta Q \rangle$ at $\beta = \beta_0$ corresponds to the temperature $\tau_0 = \frac{1}{\beta_0}$. The result

$$\langle \Delta Q \rangle = -a \,\beta_0 \,\left(\tau - \tau_0\right) + O\left(\tau - \tau_0\right)^2 \tag{61}$$

resembles the Fourier law or its precursor, Newton's law of cooling [25], stating that the rate of heat loss of a body is directly proportional to the difference in the temperatures between the body and its surroundings. We further remark that the explicit form (60) of the "heat conduction coefficient" $a \beta_0$ in (61) is reminiscent of the fluctuation-dissipation theorems mentioned in [7] in connection with the Jarzynski equation, see also Appendix B.2.

The above result that $\beta \Delta Q = \Delta S + O(\beta - \beta_0)^2$ can be viewed as a confirmation of the Clausius identity in linear stochastic thermodynamics. The fact that the deviation to the Clausius identity is non-negative in the sense of Theorem 3 can be made plausible in the following way. Consider a state change of an NLS with a slightly lower temperature than the heat bath, $\tau < \tau_0$, consisting of two steps. In the first step, there is a limited contact with the heat bath such that only the heat $\Delta_1 Q$ is flowing into the TLS leading, in linear approximation, to an increase of its entropy by $\Delta_1 S = \frac{\Delta_1 Q}{2}$. After this first step, the system, while being kept isolated, thermalizes and approximately assumes a Gibbs state with temperature τ_1 such that $\tau < \tau_1 < \tau_0$. This can be reasonably expected if *N* is large enough (or if N = 2). In a second step, there is another contact with the heat bath leading to a further heat transfer of $\Delta_2 Q$ and, in linear approximation, to an increase of its entropy by $\Delta_2 S = \frac{\Delta_2 Q}{\tau} < \frac{\Delta_2 Q}{\tau}$. The total heat transfer is $\Delta Q = \Delta_1 Q + \Delta_2 Q$ and the total increase of entropy is $\Delta S =$ $\Delta_1 S + \Delta_2 S$ which is *less* than $\frac{\Delta Q}{\tau}$. An analogous reasoning applies to the case of $\tau > \tau_0$ and a cooling of the NLS in two steps. The "first Clausius inequality" $\beta \langle \Delta O \rangle > \langle \Delta S \rangle$ thus reflects the fact that β is the fixed initial inverse temperature of the NLS and possible changes of the NLS's temperature during the interaction with the heat bath are ignored in the term $\beta(\Delta Q)$ but would be relevant for the term $\langle \Delta S \rangle$. On the other hand, the term $\beta \langle \Delta Q \rangle$ cannot be improved in a simple way, because after the interaction with the heat bath, the NLS may no longer be in a Gibbs state and thus has no temperature at all.

Next, we turn to a second Clausius inequality that can be obtained from the Jarzynski-type equation (19) by choosing $\widetilde{p}_m = q_m := \sum_n T_{mn} p_n$ for all $m \in \mathcal{N}$. This yields

$$\left\langle \frac{p_n^{(0)} q_m}{p_m^{(0)} p_n} \right\rangle = 1. \tag{62}$$

As above, we may invoke Jensen's inequality (JI) and the fact that $x \mapsto -\log x$ is a convex function:

$$0 = -\log 1 \stackrel{(62)}{=} -\log \left\langle \frac{p_n^{(0)} q_m}{p_m^{(0)} p_n} \right\rangle \tag{63}$$

$$\stackrel{(II)}{\leq} \left\langle -\log \frac{p_n^{(0)}}{d_n} + \log \frac{p_m^{(0)}}{d_m} - \log \frac{q_m}{d_m} + \log \frac{p_n}{d_n} \right\rangle \tag{64}$$

$$\stackrel{\text{(8)}}{=} \langle \beta_0 E_n + \log Z_0 - \beta_0 E_m - \log Z_0 \rangle - \sum_m q_m \log \frac{q_m}{d_m} + \sum_n p_n \log \frac{p_n}{d_n}$$
(65)

$$= \langle \Delta S \rangle - \beta_0 \langle \Delta Q \rangle, \tag{66}$$

where we have suitably expanded the fraction (63) with the factors d_n and d_m . Together with (38), we have thus proven the following

Theorem 4.

$$\beta_0 \langle \Delta Q \rangle \le \langle \Delta S \rangle \le \beta \langle \Delta Q \rangle.$$
 (67)

The second Clausius inequality $\beta_0 \langle \Delta Q \rangle \leq \langle \Delta S \rangle$ has also been obtained in [21], Eq. (4.4), under the same conditions corresponding to our Assumption 1 and using the "monotonicity of the Kullback-Leibler (KL) divergence". This proof is closely related to ours, since the said monotonicity is also a consequence of the general J-equation, see Appendix C.

Recall that according to Theorem 2, heat is always flowing from the hotter body to the colder one. According to the first Clausius inequality (38), the analogous statement for the entropy flow can only be shown in the case of $0 \le \beta \le \beta_0$, i.e., where the NLS has initially a

larger temperature than the heat bath. This follows since $\beta-\beta_0 \leq 0$ implies $\langle \Delta Q \rangle \leq 0$ by Theorem 2 and hence, $\langle \Delta S \rangle \leq \beta \langle \Delta Q \rangle \leq 0$. The second Clausius inequality in (67) can now be used to extend the statement about the entropy flow to the case of $\beta > \beta_0$, i.e., where the NLS has initially a lower temperature than the heat bath. In this case, we always have $\langle \Delta Q \rangle \ge 0$ by Theorem 2 and hence, $\langle \Delta S \rangle \ge \beta_0 \, \langle \Delta Q \rangle \ge 0$. We thus have proven the following

Theorem 5. Under the preceding conditions and for nonnegative inverse temperatures of the NLS, i.e., $\beta \ge 0$ there holds

$$(\beta - \beta_0) \langle \Delta S \rangle \ge 0. \tag{68}$$

4 Bi-stochastic limit case

As remarked in Section 2, in the limit case $\beta_0 = 0$ and if $d_n = 1$ for all $n \in \mathcal{N}$, we obtain the special case of a bistochastic transition matrix *T* satisfying (6). For $d_n \equiv 1$, the entropy (31) can be identified with the Shannon entropy [26], up to the choice of units. Physically, this case can be realized by an NLS subject to external time-dependent forces but not coupled to a heat bath. Although this special case is actually outside the thematic scope of this article, it will be instructive to investigate it closer. The mathematics we used does not presuppose $\beta_0 \neq 0$ and hence, this special case should be included in the preceding sections. According to the mentioned physical realization of the bistochastic limit case, we will refer to the random variable ΔE as "work" and denote it by the variable w.

In particular, we consider the "Clausius inequalities" (67) and re-write them as

$$0 \le \langle \Delta S \rangle \le \beta \langle w \rangle. \tag{69}$$

For $\beta \ge 0$, it implies $\langle w \rangle \ge 0$, a result that could also have been derived from the usual Jarzynski equation, see, e.g., [27].

Another consequence of (69) is $\langle \Delta S \rangle \geq 0$ (in contrast to $\langle \Delta S \rangle = 0$ for classical adiabatic work processes). This result can be independently proven as follows: every bistochastic matrix *T* can be written as a convex sum of permutational matrices. This is the Birkhoff-von Neumann theorem, see [28, 29]. The Shannon entropy is invariant under permutations, but increases under a convex sum of probability distributions. The latter is due to the concavity of the Shannon entropy, see, e.g., Ex. 11.21 in [18].

5 Analytical example

As an example where the transition matrix T can be exactly calculated, we consider a single spin with spin quantum number s = 1 coupled to a harmonic oscillator that serves as a heat bath. Hence, we have a three-level system, $\mathcal{N} =$ $\{1,0,-1\}$ and $N=|\mathcal{N}|=3$. The total Hamiltonian is

$$H = H_1 + H_2 + H_{12}, (70)$$

where

$$H_1 = s_z \otimes 1_{\text{HO}} \tag{71}$$

$$H_2 = \mathbb{I}_{\text{spin}} \otimes \sum_{n=0}^{\infty} \left(n + \frac{1}{2} \right) |n\rangle \langle n| \tag{72}$$

$$H_{12} = \lambda \left(s^{+} \otimes A + s^{-} \otimes A^{*} \right). \tag{73}$$

Here s_x, s_y, s_z are the three spin operators and $s^{\pm} =$ $s_x \pm i s_y$ the two corresponding ladder operators. Similarly, A and A^* are the lowering and raising operators, respectively, for the harmonic oscillator, such that H_2 = $\mathbb{I}_{\text{spin}} \otimes \left(A^*A + \frac{1}{2}\mathbb{I}_{\text{HO}}\right)$ and $(|n\rangle)_{n=0,1,2,\dots}$ denotes the eigenbasis of A^*A . λ is a real parameter. Further, let $(|m\rangle)_{m=1,0,-1}$ be the eigenbasis of s_z such that $(|m,n\rangle)_{m\in\mathcal{N},n\in\mathbb{N}}$ is an orthonormal basis of the total Hilbert space.

The Hamiltonian (70)–(73) strongly resembles the Jaynes-Cummings model [30], which describes the interaction of a two-level system with a quantized radiation field. The extension to three-level systems has also been considered [31-33], but always assumes non-uniform level spacings and two radiation modes.

This system is analytically solvable since H_{12} commutes with $H_1 + H_2$. The eigenspaces of $H_1 + H_2$ are, hence, left invariant under H. They are of the following form: either the singlet spanned by $|-1,0\rangle$, or the doublet spanned by $|0,0\rangle$ and $|-1,1\rangle$, or an infinite number of triplets spanned by $|1, n-1\rangle$, $|0, n\rangle$, and $|-1, n+1\rangle$, where $n = 1, 2, 3, \dots$ Within the triplets *H* has the form

$$H^{(n)} = \begin{pmatrix} n + \frac{1}{2} & \lambda\sqrt{2n} & 0\\ \lambda\sqrt{2n} & n + \frac{1}{2} & \lambda\sqrt{2n+2}\\ 0 & \lambda\sqrt{2n+2} & n + \frac{1}{2} \end{pmatrix}, \tag{74}$$

and the corresponding eigenvalues

$$E_i^{(n)} \in \left\{ n + \frac{1}{2}, n + \frac{1}{2} \pm \lambda \sqrt{4n + 2} \right\}.$$
 (75)

Let π denote a Gibbs state of the harmonic oscillator, such that

$$\pi_n = \frac{1}{7} e^{-\beta_0 \left(n + \frac{1}{2}\right)} \tag{76}$$

$$Z = \sum_{n \in \mathbb{N}} e^{-\beta_0 \left(n + \frac{1}{2}\right)} = \frac{e^{-\frac{\beta_0}{2}}}{1 - e^{-\beta_0}}.$$
 (77)

We choose as an initial mixed state

$$\rho = \sum_{mn} p_m \pi_n |mn\rangle \langle mn|, \qquad (78)$$

with an arbitrary probability distribution p. After the time t, this state will evolve into

$$\rho' = e^{-iHt} \rho e^{iHt}. \tag{79}$$

To simplify the following calculation, we will consider the *time average*

$$\rho'' = \overline{\rho'} = \overline{e^{-iHt} \rho e^{iHt}} . \tag{80}$$

The time averaged probability of finally occupying the state $r \in \mathcal{N}$ will be

$$q_r = \sum_{k} \langle rk | \rho'' | rk \rangle =: \sum_{m} T_{rm} p_m. \tag{81}$$

The latter equation follows since q_r is a linear function of p and defines the transition matrix T. From what has been said above it is clear that T will be obtained by a summation over all eigenspaces of $H_1 + H_2$. It proves to be independent of λ due to time averaging. After some computer-algebraic calculations, we obtain

$$T_{1,1} = \frac{1}{32} \left(e^{\beta_0} - 1 \right) \left(\frac{12}{e^{\beta_0} - 1} + 8 e^{\frac{\beta_0}{2}} \coth^{-1} \left(e^{\frac{\beta_0}{2}} \right) + 3 e^{-\beta_0} \Phi \left(e^{-\beta_0}, 2, \frac{3}{2} \right) - 8 \right), \quad (82)$$

$$T_{1,0} = \frac{1}{4} \left(1 - 2 \sinh\left(\frac{\beta_0}{2}\right) \tanh^{-1}\left(e^{-\frac{\beta_0}{2}}\right) \right), \quad (83)$$

$$T_{1,-1} = \frac{3}{32} e^{-3\beta_0} \left(4e^{\beta_0} - \left(e^{\beta_0} - 1 \right) \Phi \left(e^{-\beta_0}, 2, \frac{3}{2} \right) \right), \quad (84)$$

$$T_{0,1} = \frac{1}{4} e^{\beta_0} \left(1 - 2 \sinh\left(\frac{\beta_0}{2}\right) \tanh^{-1}\left(e^{-\frac{\beta_0}{2}}\right) \right),$$
 (85)

$$T_{0,0} = \frac{1}{2},\tag{86}$$

$$T_{0,-1} = \frac{1}{4} e^{-\frac{3\beta_0}{2}} \left(e^{\frac{\beta_0}{2}} + \left(e^{\beta_0} - 1 \right) \tanh^{-1} \left(e^{-\frac{\beta_0}{2}} \right) \right), \quad (87)$$

$$T_{-1,1} = \frac{3}{32} e^{-\beta_0} \left(4 e^{\beta_0} - \left(e^{\beta_0} - 1 \right) \Phi \left(e^{-\beta_0}, 2, \frac{3}{2} \right) \right), \quad (88)$$

$$T_{-1,0} = \frac{1}{4} \left(2 \sinh\left(\frac{\beta_0}{2}\right) \tanh^{-1}\left(e^{-\frac{\beta_0}{2}}\right) + 1 \right),$$
 (89)

$$T_{-1,-1} = \frac{1}{32} e^{-3\beta_0} \left(4 e^{2\beta_0} \left(11 \sinh \left(\beta_0 \right) + 5 \cosh \left(\beta_0 \right) \right) \right.$$
$$\left. - 4 \sinh \left(\frac{\beta_0}{2} \right) \coth^{-1} \left(e^{\frac{\beta_0}{2}} \right) - 2 \right)$$
$$\left. + 3 \left(e^{\beta_0} - 1 \right) \Phi \left(e^{-\beta_0}, 2, \frac{3}{2} \right) \right). \tag{90}$$

Here $\Phi(z,s,a) := \sum_{k \in \mathbb{N}} \frac{z^k}{(k+a)^s}$ denotes the Lerch's transcendent, see Section 25.14 in [34]. It can be shown that T is a left stochastic matrix and leaves the probability distribution

$$p^{(0)} = \frac{1}{e^{-\beta_0} + e^{\beta_0} + 1} \left(e^{-\beta_0}, 1, e^{\beta_0} \right)$$
(91)

invariant that corresponds to a Gibbs state with inverse temperature β_0 . It follows that Assumption 1 is satisfied and hence the results derived in Sections 2 and 3 hold for our example. We illustrate this by showing the three functions $\beta\Delta Q$, ΔS , and $\beta_0\Delta Q$ for $-5\beta_0\leq\beta\leq5\beta_0$ in Figure 3 satisfying the Clausius inequalities (67). For this example, we make the following observation, which seems to be typical for NLS coupled to a heat bath: If the three-level system is initially hotter than the heat bath, $0<\beta<\beta_0$, the maximal heat transfer $|\Delta Q|$ results for $\beta\to0$, as expected. In contrast, the entropy transfer $|\Delta S|$ takes its maximum at a positive inverse temperature $\beta_{\rm max}$, see Figure 3. This is remarkable in the sense that one might naively think that in nonequilibrium thermodynamics the identity $\Delta S=\beta_0\Delta Q$,

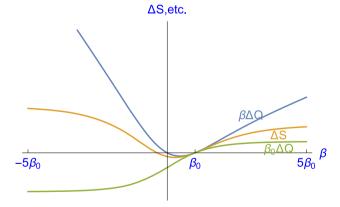


Figure 3: Plot of the two "Clausius heat terms" $\beta_0 \Delta Q$, $\beta \Delta Q$, and the "entropy increase" ΔS as functions of the inverse temperature β of the three-level system considered in Section 5 and the corresponding transition matrix T according to (82)-(90). The range of the inverse temperature β is chosen as $-5\beta_0 \leq \beta \leq 5\beta_0$ and the calculations have been done for $\beta_0 = 1$. It is remarkable that for $0 < \beta < \beta_0$, the absolute value $|\Delta S|$ has its maximum not for $\beta = 0$, as it is the case for $|\beta_0 \Delta Q|$, but for some positive inverse temperature of $\beta_{\rm max} \approx 0.279896$.

which holds for linear thermodynamics, could be weakened to a monotonic relation between ΔS and $\beta_0 \Delta O$. However, this is not correct: if one increases the temperature above $1/\beta_{\text{max}}$, the reduced heat transfer $|\beta_0 \Delta Q|$ also increases, while the entropy transfer $|\Delta S|$ decreases.

6 Summary and outlook

In this paper, we have presented an approach to the timehonored problem of the second law for a finite quantum system coupled to a heat bath. We have re-derived several known partial results, in part under weaker assumptions, and integrated them into a theory based on general Jequations. These resemble the famous Jarzynski equation and imply certain second law-like inequalities. It will be in order to provide a general survey that shows their logical dependencies, see Figure 4.

The most general I-equation is (C5), the central (red) equation of Figure 4. It holds for two sequential measurements under rather general assumptions, see Theorem 6, and contains two undetermined probability distributions \widetilde{p} and $p^{(0)}$. There are two principal specialization paths that physically correspond to "work processes" (upward direction in Figure 4) and "heat processes" (downward direction in Figure 4).

For "work processes" performed on closed systems that are only marginally touched in this paper, the transition matrix T is bi-stochastic in the modified sense of Eq. (7). This entails the J-equation (27) in [15] (the upper blue equation in Figure 4) that can be further specialized according to the choice of \widetilde{p} . The usual Jarzynski equations are derived for the choice of $\widetilde{p} = p$, whereas the alternative $\widetilde{p} = q := T p$ leads to a scenario reminiscent of earlier work of W. Pauli and F. Klein, see [15, 16].

By contrast, the "heat processes" performed on systems without external forces but under contact with a heat bath are characterized by $Tp^{(0)} = p^{(0)}$ and lead to another special J-equation (19) (the lower green equation in Figure 4) that is of central importance for this work. Again, there are two further options. The choice $\tilde{p} = p$ and the restriction to probability distribution given by Gibbs states leads to (23) and, by means of Jensen's inequality (JI), to the relation (26). The latter states that, on statistical average, heat always flows from the hot system to the cold bath and vice versa.

For the analogous statement (68) about the average flow of entropy, we additionally required the two Clausius inequalities. The first one, $\Delta S \leq \beta \Delta Q$, is a simple consequence of the Gibbs inequality (GI). The second

one, $\beta_0 \Delta Q \leq \Delta S$, follows via (JI) from the mentioned Jequation (19) and the choice $\tilde{p} = a := T p$.

In the following, we will relate our results to similar statements found in the relevant literature.

Jarzynski and Wójcik [19] consider two systems which initially have different temperatures, then interact weakly and finally (in the quantum case) are subjected to a separate energy measurement for both systems. They derive a Crooks-like equality, and from this a Jarzynski-type equation, Eq. (18) in [19] that corresponds to our Eq. (23). Important assumptions are: neglect of the interaction between both systems for the heat balance and microreversibility. In contrast, we will focus on the 1st system and describe the second one only in a general way by the transition matrix T. Our assumptions are weaker: T leaves invariant some Gibbs state without neglecting the interaction; time reversal invariance is not needed (and actually will be violated for the example presented in Section 5).

Jennings and Rudolph [20] also consider two systems, which, however, can also be initially entangled. The special case, which is interesting for our purposes, is that both systems are uncorrelated at the beginning and have different temperatures. A first Clausius inequality, corresponding to our (38), is derived from the property that the Gibbs state minimizes the free energy. From this directly, without using a Jarzynski-type equation, the heat flow inequality, Eq. (3) in [20], follows, which corresponds to our Eq. (26), but again assuming, as in [19], that the amount of heat emitted by the first system is exactly absorbed by the second one.

The second Clausius inequality that appears in our (67), can also be found in Chapter 4.1 of [21], and is proved there via the "monotonicity of the KL divergence". This proof is closely related to ours, since the said monotonicity follows from the general J-equation, see Appendix C. The following statements in [21] interpreting the second Clausius inequality as a form of the second law of stochastic thermodynamics should be taken with some caution, see the discussion above.

Another related result has been proven already in 1978 by Spohn [22]: for an open quantum mechanical system described by a quantum dynamical semigroup that leaves invariant a certain state ρ^0 , the *entropy production* is nonnegative. The latter is defined as the time derivative of the KL divergence between ρ_t and ρ^0 . This result has been recently reformulated in [23] in a way compatible with our approach; Eqs. (16) and (17) of that reference immediately imply the second Clausius inequality.

Summarizing the state of research, partial formulations of the second law for the coupling of an NLS to a heat bath can be found to a sufficient extent in recent years,

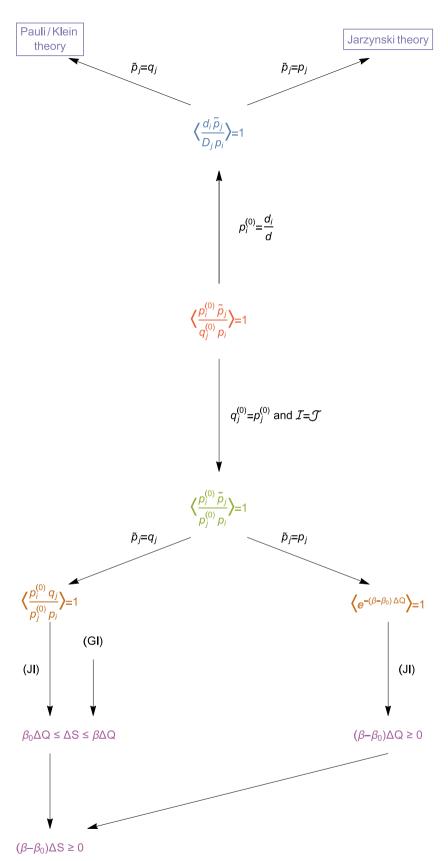


Figure 4: Schematic representation of various forms of J-equations and inequalities and their logical dependencies. Detailed explanations are given in Section 4.

but they have to be integrated into a unified theory and proved under conditions as weak as possible. This has been attempted in the present work.

Moreover, we have presented an analytically solvable example illustrating our approach. It consists of a three-level system (a spin with s=1) coupled to a harmonic oscillator. For this example, our central Assumption 1, saying that the transition matrix has a fixed point of Gibbs type, is exactly satisfied. It would be a task for the future to investigate the conditions under which this assumption holds exactly or approximately.

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Appendix A: Proof of Proposition 1

First, we will calculate the energy increase in the weak coupling limit:

$$\Delta E = E(T\,p) - E(p) = \sum_{m} T_{mn}\,p_n\,E_m - \sum_{m} p_n\,E_n \qquad (A1)$$

$$\stackrel{(45)}{=} \varepsilon \sum_{mn} t_{mn} p_n E_m + O\left(\varepsilon^2\right). \tag{A2}$$

Recall that the (left) stochasticity of *T* implies

$$\sum_{m} t_{mn} = 0. \tag{A3}$$

Further,

$$\left. \frac{\partial}{\partial q_m} S(q) \right|_{q=p} = -\frac{\partial}{\partial q_m} \sum_n q_n \log \frac{q_n}{d_n} \bigg|_{q=p}$$

$$-\left(1 + \log \frac{p_m}{d_m} \right) \tag{A4}$$

and hence,

$$\left. \varepsilon \left. \frac{\partial}{\partial \varepsilon} S(q) \right|_{\varepsilon=0} = \varepsilon \left. \sum_{m} \frac{\partial q_{m}}{\partial \varepsilon} \frac{\partial}{\partial q_{m}} S(q) \right|_{q=n}$$
 (A5)

$$\stackrel{\text{(45,A4)}}{=} - \varepsilon \sum_{m} \left(\sum_{n} t_{mn} p_{n} \right) \left(1 + \log \frac{p_{m}}{d_{m}} \right) \tag{A6}$$

$$\stackrel{\text{(A3)}}{=} -\varepsilon \sum_{m} \left(\sum_{n} t_{mn} p_{n} \right) \log \frac{p_{m}}{d_{m}} \tag{A7}$$

$$\stackrel{(1)}{=} \varepsilon \sum_{mn} t_{mn} \, p_n \, \left(\beta E_m + \log Z \right) \tag{A8}$$

$$\stackrel{\text{(A3)}}{=} \varepsilon \beta \sum_{mn} t_{mn} p_n E_m \tag{A9}$$

$$\stackrel{\text{(A1)}}{=} \beta \, \Delta E + O\left(\varepsilon^2\right). \tag{A10}$$

Finally,

$$\Delta S = \varepsilon \left. \frac{\partial}{\partial \varepsilon} S(q) \right|_{\varepsilon=0} + O\left(\varepsilon^2\right) = \beta \, \Delta E + O\left(\varepsilon^2\right), \quad \text{(A11)}$$

which completes the proof of Proposition 1.

Appendix B: Proof of $a \ge 0$

We will present two proofs of the fact that the slope a of $\beta_0 \langle \Delta Q \rangle$ considered as a function of β will be non-negative at $\beta = \beta_0$.

B.1 First proof

We write a as double sum according to (60) and add the same sum but with n and m interchanged. This yields

$$a = \frac{\beta_0}{2} \sum_{nm} \left(T_{nm} \, p_m^{(0)} \, E_m - T_{mn} \, p_n^{(0)} \, E_n \right) (E_m - E_n) \,. \tag{B1}$$

Using

$$T_{nm} p_m^{(0)} = \frac{1}{2} \left(T_{nm} p_m^{(0)} + T_{mn} p_n^{(0)} \right) + \frac{1}{2} \left(T_{nm} p_m^{(0)} - T_{mn} p_n^{(0)} \right), \tag{B2}$$

and the analogous expression for $T_{mn}\,p_n^{(0)}$, we obtain

$$a = \frac{\beta_0}{4} \sum_{nm} \left(\left(T_{nm} \, p_m^{(0)} + T_{mn} \, p_n^{(0)} \right) E_m \, (E_m - E_n) \right.$$
$$+ \left(T_{nm} \, p_m^{(0)} - T_{mn} \, p_n^{(0)} \right) E_m \, (E_m - E_n)$$

$$-\left(T_{mn}\,p_n^{(0)} + T_{nm}\,p_m^{(0)}\right)E_n\left(E_m - E_n\right)$$
$$-\left(T_{mn}\,p_n^{(0)} - T_{nm}\,p_m^{(0)}\right)E_n\left(E_m - E_n\right) \tag{B3}$$

$$= \frac{\beta_0}{4} \sum_{nm} \left(\left(T_{nm} p_m^{(0)} + T_{mn} p_n^{(0)} \right) (E_m - E_n)^2 + \left(T_{nm} p_m^{(0)} - T_{mn} p_n^{(0)} \right) (E_m^2 - E_n^2) \right)$$
(B4)

The first term in (B4) is non-negative and the second one vanishes according to

$$\sum_{nm} \left(T_{nm} \, p_m^{(0)} - T_{mn} \, p_n^{(0)} \right) E_m^2$$

$$= \sum_{nm} \left(p_m^{(0)} \, E_m^2 - p_m^{(0)} \, E_m^2 \right) = 0, \tag{B5}$$

and

$$\sum_{nm} \left(T_{nm} \, p_m^{(0)} - T_{mn} \, p_n^{(0)} \right) E_n^2$$

$$= \sum_n \left(p_n^{(0)} \, E_n^2 - p_n^{(0)} \, E_n^2 \right) = 0. \tag{B6}$$

Here, we have used T that is left stochastic, see (5), and leaves $p^{(0)}$ fixed, see (10), according to Assumption 1.

B.2 Second proof

The second proof is based on the cumulant expansion for a random variable *X*, see, e.g., 26.1.12 in [35],

$$\log \left\langle e^{tX} \right\rangle = \sum_{n=1}^{\infty} \kappa_n \frac{t^n}{n!} = \langle X \rangle t + \frac{1}{2} \sigma^2(X) t^2 + \cdots, \quad (B7)$$

defining the cumulants

$$\kappa_1 = \langle X \rangle, \quad \kappa_2 = \sigma^2(X) := \langle X^2 \rangle - \langle X \rangle^2, \quad (B8)$$

$$\kappa_3 = \langle (X - \langle X \rangle)^3 \rangle, \dots$$
(B9)

In our case, we set $X = \Delta Q$ and $t = -(\beta - \beta_0)$ and use Eq. (23) to obtain

$$0 = \log 1 \stackrel{(23)}{=} \log \left\langle e^{-(\beta - \beta_0)\Delta Q} \right\rangle \stackrel{(B7)}{=} - \left\langle \Delta Q \right\rangle (\beta - \beta_0)$$
$$+ \frac{1}{2} \sigma^2 (\Delta Q) (\beta - \beta_0)^2 + O(\beta - \beta_0)^3. \tag{B10}$$

Hence,

$$\beta_0 \langle \Delta Q \rangle = \frac{\beta_0}{2} \sigma^2 (\Delta Q) (\beta - \beta_0) + O(\beta - \beta_0)^2.$$
 (B11)

This proves that $a = \frac{\beta_0}{2} \sigma^2(\Delta Q) \ge 0$ since the variance $\sigma^2(...)$ of every random variable is non-negative.

Appendix C: General J-equation

We will sketch the general probabilistic framework, analogous to that in [15] and already used in Section 2 for a special case. It deals with two sequential measurements and the corresponding general J-equation. We have two

sets of outcomes, \mathcal{I} for the first and \mathcal{J} for the second measurement. Further, there exists a probability distribution

$$P: \mathcal{I} \times \mathcal{J} \to [0, 1]$$
 (C1)

of the form

$$P(i, j) = T_{ii} p_i, \quad i \in \mathcal{I} \text{ and } j \in \mathcal{J},$$
 (C2)

where T is a (left) stochastic matrix and $p: \mathcal{I} \to [0, 1]$ a probability distribution. *P* will be used to calculate expectation values $\langle Y \rangle$ for random variables $Y: \mathcal{I} \times \mathcal{J} \to \mathbb{R}$.

For simplicity, we assume that \mathcal{I} and \mathcal{J} are finite and $p_i > 0$ for all $i \in \mathcal{I}$. Let $\widetilde{p}: \mathcal{J} \to [0,1]$ and $p^{(0)}: \mathcal{I} \to (0,1)$ be two further probability distributions and define

$$q_j := \sum_i T_{ji} p_i, \quad j \in \mathcal{J}$$
 (C3)

$$q_j^{(0)} := \sum_i T_{ji} p_i^{(0)}, \quad j \in \mathcal{J}.$$
 (C4)

Then, the following holds.

Theorem 6. (General J-equation)

$$\left\langle \frac{p_i^{(0)}\,\widetilde{p}_j}{q_j^{(0)}\,p_i} \right\rangle = 1. \tag{C5}$$

Proof.

$$\left\langle \frac{p_i^{(0)} \tilde{p}_j}{q_i^{(0)} p_i} \right\rangle = \sum_{ij} P(i,j) \frac{p_i^{(0)} \tilde{p}_j}{q_i^{(0)} p_i} \tag{C6}$$

$$\stackrel{\text{(C2)}}{=} \sum_{ij} T_{ji} \,_{i} \, \frac{p_{i}^{(0)} \, \widetilde{p}_{j}}{q_{i}^{(0)} \,_{i}} \tag{C7}$$

$$\stackrel{\text{(C4)}}{=} \sum_{j} \stackrel{\text{(0)}}{\stackrel{\text{(0)}}{=}} \frac{\widetilde{p}_{j}}{\stackrel{\text{(0)}}{=}} = \sum_{j} \widetilde{p}_{j} = 1.$$

$$\square$$

The general J-equation (C5) is more of a template that can be used to generate further equations by choosing a special form of the general probability distribution \widetilde{p} . Note that it is not required that the probability distribution $p^{(0)}$ is invariant under T; if this is the case and, moreover, $\mathcal{I} = \mathcal{J} \equiv \mathcal{N}$ then the special form of Eq. (19) results.

The J-equation (27) in [15] follows for the choice of $p_i^{(0)} = \frac{d(i)}{d}$ for all $i \in \mathcal{I}$, where $d := \sum_i d(i)$ that leads to a modified bi-stochasticity of *T* in the sense of Eq. (25) in [15].

As for every Jarzynski-type equation, the application of Jensen's inequality (JI) using the concave function $x \mapsto \log x$ yields a second law-like inequality. In the case of (C5), this inequality turns out to be equivalent to the

"monotonicity of the KL divergence", see [21], if we set $\widetilde{p}_i = q_i$ for all $j \in \mathcal{J}$. This will be shown in the following.

$$0 = \log 1 \stackrel{\text{(C5)}}{=} \log \left\langle \frac{p_i^{(0)} q_j}{q_i^{(0)} p_i} \right\rangle \tag{C9}$$

$$\stackrel{\text{(II)}}{\geq} \left\langle \log \frac{p_i^{(0)} q_j}{q_j^{(0)} p_i} \right\rangle \tag{C10}$$

$$= \left(\left\langle \log \, q_j \right\rangle - \left\langle \log \, q_j^{(0)} \right\rangle \right)$$

$$-\left(\langle \log p_i \rangle - \left\langle \log p_i^{(0)} \right\rangle\right).$$
 (C11)

We further obtain

$$\langle \log q_j \rangle = \sum_{ij} T_{ji} p_i \log q_j = \sum_i q_j \log q_j,$$
 (C12)

and

$$\left\langle \log q_j^{(0)} \right\rangle = \sum_{ij} T_{ji} p_i \log q_j^{(0)} = \sum_j q_j \log q_j^{(0)},$$
 (C13)

hence,

$$\left\langle \log q_j \right\rangle - \left\langle \log q_j^{(0)} \right\rangle = \sum_j q_j \log \frac{q_j}{q_j^{(0)}} = S\left(q \| q^{(0)}\right). \tag{C14}$$

Analogously,

$$\langle \log p_i \rangle - \left\langle \log p_i^{(0)} \right\rangle = \sum_i p_i \log \frac{p_i}{p_i^{(0)}} = S\left(p \| p^{(0)}\right), \tag{C15}$$

and hence, (C10) is equivalent to the monotonicity of the KL-divergence written as

$$S(q||q^{(0)}) \le S(p||p^{(0)}).$$
 (C16)

As mentioned in Section 1, the general J-equation belongs to the framework of stochastic thermodynamics and is as such neither quantum nor classical. Nevertheless, it will be instructive to sketch realizations of the framework in these two domains.

We begin with the quantum domain. Consider a finitedimensional system Σ_1 initially described by a statistical operator with spectral decomposition $\rho_1 = \sum_i x_i P_i$ such that

$$1 = \operatorname{Tr} \rho_1 = \sum_i x_i \operatorname{Tr} P_i =: \sum_i x_i d_i =: \sum_i p_i.$$
 (C17)

In the example studied in this paper, the P_i would be the eigenprojections of the Hamiltonian H and the x_i the corresponding eigenvalues of $\frac{1}{Z} \exp(-\beta H)$.

A first projective measurement corresponding to the complete family of mutually orthogonal projections $(P_i)_{i\in\mathcal{I}}$

leaves ρ_1 invariant. The system is then coupled to some auxiliary system Σ_2 with initially mixed state ρ_2 and the total system undergoes a finite time evolution described by some unitary operator U defined in the total Hilbert space. Finally, a quantum measurement at Σ_1 is performed corresponding to a complete family of mutually orthogonal projections $(Q_j)_{j \in \mathcal{I}}$. The probability q_j of the outcome $j \in \mathcal{I}$ \mathcal{J} of the final measurement is given by

$$q_{j} = \operatorname{Tr}\left(\left(Q_{j} \otimes \mathbb{1}\right) U\left(\rho_{1} \otimes \rho_{2}\right) U^{*}\right) \tag{C18}$$

$$= \sum_{i} p_{i} \operatorname{Tr} \left(\left(Q_{j} \otimes \mathbb{1} \right) U \left(\frac{P_{i}}{d_{i}} \otimes \rho_{2} \right) U^{*} \right) \tag{C19}$$

$$=: \sum_{i} T_{ji} p_{i}. \tag{C20}$$

It is straightforward to check that the matrix *T* defined by (C20) is (left) stochastic using $\sum_{i} Q_{i} = 1$.

We note that it is not necessary to take the total initial state as a product state $\rho_1 \otimes \rho_2$, although this is usually assumed in the literature on the second law, e.g., in p. 113 of [1], or pp. 230602-3 of [19], and also in this paper, see Section 2. But if we assume an arbitrary total initial state ρ and perform the first projective measurement according to the family $(P_i \otimes 1)_{i \in I}$, then the resulting state will be $\rho' = \sum_{i \in \mathcal{I}} (P_i \otimes 1) \rho (P_i \otimes 1)$, which is not entangled but may, nevertheless, have some "classical" correlation. It yields the initial probabilities $p_i = \text{Tr}(P_i \otimes 1) \rho$ and

$$q_{j} = \operatorname{Tr}\left(\left(Q_{j} \otimes \mathbb{1}\right) U\left(\sum_{i} p_{i} \frac{\left(P_{i} \otimes \mathbb{1}\right) \rho \left(P_{i} \otimes \mathbb{1}\right)}{\operatorname{Tr}\left(P_{i} \otimes \mathbb{1}\right) \rho}\right) U^{*}\right) \tag{C21}$$

$$=: \sum_{i} T_{ji} p_i, \tag{C22}$$

analogously to (C20).

In the classical case, we work with a phase space $(\mathcal{P}, d\mu)$ and an initial probability density ρ satisfying

$$\int_{p} \rho \, \mathrm{d}\mu = 1. \tag{C23}$$

The phase space is decomposed according to the finite partition $\mathcal{P} = \biguplus_{i \in \mathcal{I}} \mathcal{P}_i$ and ρ is correspondingly written as

$$\rho = \sum_{i} \chi_{i} \rho = \sum_{i} p_{i} \rho_{i}, \tag{C24}$$

where

$$p_i := \int_{p_i} \rho \, \mathrm{d}\mu \;, \quad \rho_i := \frac{\chi_i \, \rho}{p_i}, \tag{C25}$$

and χ_i is the characteristic function of \mathcal{P}_i for all $i \in \mathcal{I}$. The time evolution of the classical system is described by a measure-preserving map $U: \mathcal{P} \to \mathcal{P}$, such that ρ will be

transformed into $\rho' = \rho \circ U^{-1}$. Finally, a discrete measurement is performed according to another finite partition $\mathcal{P} = \biguplus_{i \in \mathcal{I}} \mathcal{Q}_i$. The probability q_i of finding the system in the subset Q_i is given by

$$q_j = \int_{\mathcal{Q}_j} \rho' \, \mathrm{d}\mu = \sum_i p_i \int_{\mathcal{Q}_i} \rho_i \circ U^{-1} \, \mathrm{d}\mu =: \sum_i T_{ji} \, p_i. \quad (C26)$$

It is straightforward to check that the matrix *T* defined by (C26) is (left) stochastic.

References

- [1] H. Spohn and J. L. Lebowitz, "Irreversible thermodynamics for quantum systems weakly coupled to thermal reservoirs," in Advances in Chemical Physics: For Ilya Prigogine, Vol. 38, S. A. Rice, Ed., Hoboken, New Jersey, John Wiley & Sons, 1987.
- [2] J. L. Lebowitz and H. Spohn, "A Gallavotti-Cohen-type symmetry in the large deviation functional for stochastic dynamics," J. Stat. Phys., vol. 95, nos. 1/2, pp. 333-365,
- [3] C. Jarzynski, "Nonequilibrium equality for free energy differences," Phys. Rev. Lett., vol. 78, no. 17, p. 2690, 1997.
- [4] J. Kurchan, "A quantum fluctuation theorem," 2000, arXiv:0007360v2 [cond-mat.stat-mech].
- [5] H. Tasaki, "Jarzynski relations for quantum systems and some applications," 2000, arXiv:0000244v2 [cond-mat.stat-mech].
- [6] S. Mukamel, "Quantum extension of the Jarzynski relation: analogy with stochastic dephasing," Phys. Rev. Lett., vol. 90, no. 17, p. 170604, 2003.
- [7] P. Talkner, M. Morillo, J. Yi, and P. Hänggi, "Statistics of work and fluctuation theorems for microcanonical initial states," New J. Phys., vol. 15, 2013, Art no. 095001.
- [8] T. Schmiedl and U. Seifert, "Stochastic thermodynamics of chemical reaction networks," J. Chem. Phys., vol. 126, 2007, Art no. 044101.
- [9] K. Saito and Y. Utsumi, "Symmetry in full counting statistics, fluctuation theorem, and relations among nonlinear transport coefficients in the presence of a magnetic field," Phys. Rev. B, vol. 78, p. 115429, 2008.
- [10] D. Andrieux, P. Gaspard, T. Monnai, and S. Tasaki, "The fluctuation theorem for currents in open quantum systems," New J. Phys., vol. 11, 2009, Art no. 043014. Erratum in: New J. Phys. 11, 109802 (2009).
- [11] J. Yi, P. Talkner, and M. Campisi, "Nonequilibrium work statistics of an Aharonov-Bohm flux," Phys. Rev. E, vol. 84, 2011, Art no. 011138.
- [12] M. Esposito, "Stochastic thermodynamics under coarse graining," Phys. Rev. E, vol. 85, 2012, Art no. 041125.
- [13] J. Yi, Y. W. Kim, and P. Talkner, "Work fluctuations for Bose particles in grand canonical initial states," Phys. Rev. E, vol. 85, 2012, Art no. 051107.
- [14] M. Campisi, P. Hänggi, and P. Talkner, "Colloquium: quantum fluctuation relations: foundations and applications," Rev. Mod. Phys., vol. 83, pp. 771-791, 2011. Erratum: Rev. Mod. Phys. 83, 1653 (2011).

- [15] H.-J. Schmidt and J. Gemmer, "A framework for sequential measurements and general Jarzynski equations," Z. Naturforsch., vol. 75, no. 3, pp. 265-284, 2020.
- [16] H.-J. Schmidt and J. Gemmer, "Sequential measurements and entropy," J. Phys.: Conf. Ser., vol. 1638, 2020, Art no. 012007.
- [17] J. von Neumann, Mathematische Grundlagen der Quantenmechanik, Berlin, Springer-Verlag, 1932. English translation: Mathematical Foundations of Quantum Mechanics, Princeton, Princeton University Press, 1955.
- [18] M. A. Nielsen and I. L. Chuang, Quantum Computation and Quantum Information, Cambridge, Cambridge University
- [19] C. Jarzynski and D. K. Wójcik, "Classical and quantum fluctuation theorems for heat exchange," Phys. Rev. Lett., vol. 92, no. 23, p. 230602, 2004.
- [20] D. Jennings and T. Rudolph, "Entanglement and the thermodynamic arrow of time," Phys. Rev. E, vol. 81, 2010, Art no. 061130.
- [21] T. Sagawa, "Entropy, divergence, and majorization in classical and quantum thermodynamics," 2020, arXiv:2007.09974v3 [quant-ph].
- [22] H. Spohn, "Entropy production for quantum dynamical semigroups," J. Math. Phys., vol. 19, no. 5, pp. 1227-1230,
- [23] T. Aoki, Y. Matsuzaki, and H. Hakoshima, "Total thermodynamic entropy production rate of an isolated quantum system can be negative for the GKSL-type Markovian dynamics of its subsystem," 2021, 2103.05308v1 [quant-ph].
- [24] H.-J. Schmidt and J. Schnack, "Analytical results on the thermalization of a large spin system," 2021, in preparation.
- Anonymous, "Scala graduum caloris. Calorum descriptiones & signa," Phil. Trans., vol. 22, no. 270, pp. 824-829, 1701.
- [26] C. E. Shannon, "A mathematical theory of communication," Bell System Tech. J., vol. 27, no. 3, pp. 379-423,
- [27] H.-J. Schmidt, "Periodic thermodynamics of a two spin Rabi model," I. Stat. Mech., vol. 2020, 2020, Art no. 043204.
- [28] G. Birkhoff, "Three observations on linear algebra," Univ. Nac. Tucumán Rev. Ser. A, vol. 5, pp. 147-151, 1946.
- [29] J. von Neumann, "A certain zero-sum two-person game equivalent to an optimal assignment problem," Ann. Math. Stud., vol. 28, pp. 5-12, 1953.
- [30] E. T. Jaynes and F. W. Cummings, "Comparison of quantum and semiclassical radiation theories with application to the beam maser," Proc. IEEE, vol. 51, no. 1, pp. 89-109, 1963.
- [31] C. C. Gerry and J. H. Eberly, "Dynamics of a Raman coupled model interacting with two quantized cavity fields," Phys. Rev. A, vol. 42, no. 11, pp. 6805-6815, 1990.
- [32] M. Alexanian and S. K. Bose, "Unitary transformation and the dynamics of a three-level atom interacting with two quantized field modes," Phys. Rev. A, vol. 52, no. 3, pp. 2218-2224,
- [33] B. T. Torosov, S. Longhia, and G. D. Vallea, "Mixed Rabi Jaynes - Cummings model of a three-level atom interacting with two quantized fields," Opt. Commun., vol. 346, pp. 110-114, 2015.

- [34] F. W. J. Olver, A. B. O. Daalhuis, D. W. Lozier, et al., Eds., NIST Digital Library of Mathematical Functions, 2021. Available at: http://dlmf.nist.gov/, Release 1.1.1 of 2021-03-15.
- [35] M. Abramowitz and I. A. Stegun, Eds. Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables, 9th printing, New York, Dover, 1972.