Thermodynamics of nonequilibrium systems with uncertain parameters

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In the real world, one almost never knows the parameters of a thermodynamic process to infinite precision. Reflecting this, here we investigate how to extend stochastic thermodynamics to systems with uncertain parameters, including uncertain number of heat baths / particle reservoirs, uncertainty in the precise values of temperatures / chemical potentials of those reservoirs, uncertainty in the energy spectrum, uncertainty in the control protocol, etc. We formalize such uncertainty with an (arbitrary) probability measure over all transition rate matrices satisfying local detailed balance. This lets us define the effective thermodynamic quantities by averaging over all LDB-obeying rate matrices. We show that the resultant effective entropy violates the second law of thermodynamics. In contrast to the effective entropy though, the expected stochastic entropy, defined as the ensemble average of the effective trajectory-level entropy, satisfies the second law. We then and explicitly calculate the second-order correction to the second law for the case of one heat bath with uncertain temperature. We also derive the detailed fluctuation theorem for expected effective trajectory entropy production for this case, and derive a lower bound for the associated expected work. Next, to ground these formal considerations with experimentally testable bounds on allowed energetics, we derive a bound on the maximal work that can be extracted from systems with arbitrarily uncertain temperature. We end by extending previous work on “thermodynamic value of information”, to allow for uncertainty in the time-evolution of the rate matrix.

I. INTRODUCTION

The microscopic laws of classical and quantum physics provide us a parameterized set of equations that specify the evolution of a closed system starting from a specific state. To use those equations we need to know that specific state, we need to be sure the system is closed, and we need to know the values of the parameters in the equations. \[?\]

Unfortunately, in very many real-world scenarios, we are uncertain about the precise state of the system, and very often the system is open rather than closed, subject to uncertain interactions with the external environment. Statistical physics captures these two types of uncertainty by building on the microscopic laws of physics in two ways. First, to capture uncertainty about the state of the system, in statistical physics we replace exact specification of the system’s state with a probability distribution over states. Second, to capture uncertain interactions between the system and the external environment, we add randomness to the dynamics, in a precisely parameterized form \[12\].

In particular, in classical stochastic thermodynamics \[18, 25\], we model the system as a probability distribution evolving under a continuous-time Markov chain (CTMC), with a precisely specified rate matrix. Typically we require that the CTMC obeys local detailed balance (LDB). This means that the rate matrix of the CTMC has to obey certain restrictions which are parameterized by the energy spectrum of the system, the number of thermodynamic reservoirs in the external environment perturbing the system’s dynamics, and the temperatures and chemical potentials of those reservoirs. Often we also allow the rate matrix of the CTMC to change in time, subject to those restrictions, according to a precisely defined “protocol”.

However, in addition to uncertainty about the state of the system, and uncertainty about interactions with the external environment, there is an additional unavoidable type of uncertainty in all real-world systems: uncertainty about the parameters in the equations governing the dynamics. In the context of stochastic thermodynamics, this means that even if we impose LDB, we will never know the reservoir temperatures and chemical potentials to infinite precision (often even being unsure about the number of such reservoirs), we will never know the energy spectrum to infinite precision, and more generally we will never know the rate matrix and its time-dependence to infinite precision.

In this paper we consider how stochastic thermodynamics (and nonequilibrium statistical physics more generally) needs to be modified to capture this third type of uncertainty, in addition to the two types of uncertainty it already captures. We emphasize that this third type of uncertainty, concerning the parameters of the thermodynamic process, is unavoidable in essentially all real-world scenarios. Nonetheless, almost nothing is known about its thermodynamic consequences \[13\].

To clarify our precise focus in this paper, we note that there has been some preliminary research on how to mod-
ify stochastic thermodynamics in the case that we, the experimentalist, are not able to view all state transitions in the system as it evolves \([2, 20]\). In contrast to our focus, this uncertainty concerns what is observed as the system evolves, whereas the uncertainty we consider involves the parameters governing that evolution. Similarly, some models consider either spatial \([11]\) or temporal \([6]\) variation of temperature and other parameters, but they assume that this evolution is known.

Probably the closest research to what we consider in this paper is sometimes called superstatistics. It has long been known that an average over Gibbs distributions cannot be written as some single Gibbs distribution (Thm. 1 in \([26]\)). This means that even equilibrium statistical physics must be modified when there is uncertainty in the temperature of a system. The analysis of these modifications was begun by Beck and Cohen \([1]\), who developed an effective theory for thermodynamics with temperature fluctuations. They considered a system coupled to a bath, which is in a local equilibrium with temperature fluctuations. They assumed that the actual rate matrix, whatever it is, satisfies LDB. In Section IV, we consider the special case where we know for certain that there is a single (heat) reservoir, but are uncertain about its temperature, which is constant during the evolution of the system. The uncertainty in temperature implies uncertainty in the transition rate matrix, since we mean as-}

\[
\beta = \int \beta f(\beta) \exp(-\beta E) \ d\beta
\]

The resulting superstatistical distribution \(p(E) = \int \beta f(\beta) \exp(-\beta E)\) was later identified with the distribution corresponding to generalized entropic functionals \([7, 8]\). Later interpretations of superstatistics were not based on the notion of local equilibria but rather on the Bayesian approach to systems with uncertain temperature \([3, 17]\). These are conceptually closer to the focus of this paper.

The rest of the paper is organized as follows: in the next section, we introduce necessary notation and briefly recall the main results of stochastic thermodynamics. In Section III, we present the general framework of expected thermodynamics for systems with uncertain transition rates. First we note that the expected probability distribution is not Markovian. We then show that the expected entropy does not satisfy the second law. On the other hand, the expected stochastic entropy, defined as the ensemble average of the expected trajectory entropy, does satisfy the second law.

For the remainder of the paper, we focus on the simple case where we know for certain that there is a single (heat) reservoir, but are uncertain about its temperature, which is constant during the evolution of the system. The uncertainty in temperature implies uncertainty in the transition rate matrix, since we mean as-}
ular reservoirs:

\[ \dot{Q}(t) = \sum_{\nu} \dot{Q}_{\nu}(t) \]

(1)

\[ = \sum_{\nu} \sum_{x} (\epsilon_{x}(t) - \mu_{\nu} n_{x}) K_{x,x'}^{\nu} P_{x'}(t) \]

(2)

where \( n_{x} \) is the number of particles in the system, as specified by the state \( x \). (For simplicity, we ignore the possibility of more than one distinguishable type of particle.) The chemical work is then given by \( W_{\text{chem}} = \sum_{\nu} \sum_{x} P_{x}(t) \mu_{\nu} n_{x} \). The Shannon entropy is written as

\[ S = -\sum_{x} P_{x} \ln P_{x}. \]

The second law of thermodynamics can be expressed as \( \dot{S} = \dot{S}_{t} + \dot{S}_{e} \) where \( \dot{S}_{t} \geq 0 \) and \( \dot{S}_{e} = \sum_{\nu} \beta_{\nu} \dot{Q}_{\nu} \).

Throughout this paper, for simplicity we assume that any time-extended thermodynamic process we refer to occurs in some interval \([t_{i}, t_{f}]\) where we have no uncertainty about those starting and ending times. We write a generic stochastic trajectory across that interval as \( x(t) \).

So the stochastic energy at time \( t \) is \( \epsilon(t) = \epsilon_{x(t)} \), and the first law of thermodynamics on the trajectory level for any time \( t \) is

\[ \dot{w}(t) = \sum_{x} \delta_{x,x(t)} \dot{\epsilon}_{x(t)}, \]

(3)

\[ \dot{q}(t) = \sum_{\nu} \dot{q}_{\nu}(t) = \sum_{\nu} \delta_{x,x(t)} (\epsilon_{x(t)} - \mu_{\nu} n_{x(t)}), \]

(4)

\[ \dot{w}_{\text{chem}}(t) = \sum_{\nu} \delta_{x,x(t)} \mu_{\nu} n_{x(t)} \]

(5)

are called the stochastic work, stochastic heat, and stochastic chemical work, respectively.

As usual, the stochastic entropy along a trajectory is defined as \( s_{x(t)} = -\ln P_{x(t)} \). Stochastic entropy production is then

\[ \dot{s}_{t} = \dot{s} - \dot{s}_{e} \]

(6)

where due to LDB, \( \dot{s}_{e} = \sum_{\nu} \beta_{\nu} \dot{q}_{\nu} \). Due to LDB, stochastic entropy production fulfills the detailed fluctuation theorem.

\[ P(\Delta s_{t})/P(-\Delta s_{t}) = e^{\Delta s_{t}}, \]

where \( P \) denotes the probability under a time-reversed protocol. By averaging these trajectory-level quantities over all trajectories, we recover the ensemble-level versions. For more details, see the Appendix.

III. EFFECTIVE THERMODYNAMICS OF THE SYSTEM WITH UNCERTAIN TRANSITION RATES

As described in the introduction, we are interested in how the conventional laws of stochastic thermodynamics concerning the evolution of a system change when there is uncertainty about the parameters of that evolution, but we assume LDB holds, whatever those parameters are. We start with comments on the general case where the transition rates of the systems are not known with infinite precision. Such uncertainty must arise whenever we do not know exact number of heat reservoirs, their temperatures and or chemical potentials, but can even arise when we do know those quantities exactly, and even when we impose LDB. (For simplicity, we not consider uncertainty in the energy spectrum or how it varies in time. [14]) However, note even if we knew those quantities to infinite precision, LDB does not uniquely fix the rate matrix \( K \), and so there can still be uncertainty concerning \( K \).

In the Appendix, we review why the general form of a transition matrix satisfying LDB can be written as

\[ K(N; \theta, R) = \sum_{\nu} K_{\nu}(\theta_{\nu}, R_{\nu}) \]

(7)

where each \( R_{\nu} \) is an arbitrary symmetric matrix and the associated \( \Pi_{\nu} \) is a diagonal matrix whose diagonal elements are the entires in the equilibrium distribution of the reservoir \( \nu \).

We now consider a probability measure \( dF_{K} \) over the rate matrices obeying Eq. (7), which quantifies our uncertainty about the temperatures / chemical potential of the reservoirs, number of reservoirs, etc. We suppose that before a system starts to evolve, its rate matrix is generated by sampling \( dF_{K} \), and that the system then evolves with that rate matrix, without ever again sampling \( dF_{K} \). However, the experimentalist is still uncertain what that randomly generated rate matrix is as they observe the system evolving. We emphasize that this scenario differs from one where the system couples / decouples from the reservoirs in a random process, or where the reservoirs undergo temperature fluctuations during its evolution, as for example as considered in superstatistics [1].

We write the associated effective value of a (perhaps implicitly time-dependent) generic quantity \( X^{K} \) as

\[ \overline{X} = \int dF_{K} X^{K} \]

(8)

where \( P_{N} \) is the probability distribution over the number of reservoirs and \( f^{N}(\theta, R) \) is the distribution over all possible LDB-obeying rate matrices for a system coupled with \( N \) reservoirs. We use the term “effective value” to refer to expectations formed this way by integrating over all possible values of \( N, \theta, R \). We instead use the term average value to mean expectations formed by integrating over all possible ensemble trajectories, and denote such a value generically as \( \langle \cdot \rangle \).

We emphasize that there are other types of uncertainty concerning thermodynamic parameters, reflecting imperfect knowledge of energy levels, chemical potentials, the control protocol driving the energy spectrum, etc. For
simplicity, in this paper we do not consider these other types of parameter uncertainty. However, it is straightforward to generalize some of the results below to capture these other types of uncertainty as well.

Using this notation, the effective distribution at any time \( t \) is
\[
\bar{p}_x(t) := \int dF_K p^K_x(t) .
\] (9)
and the time evolution of \( \bar{p} \) is given by
\[
\dot{\bar{p}}_x(t) = \sum_{x'} \mathbf{J}_{x,x'} = \sum_{x'} \int dF_K K_{x,x'} p^K_x(t) .
\] (10)

The corresponding transition matrix at time \( t \) can be formally defined as
\[
K_{x,x'}(p^K(t)) := \frac{\int dF_K K_{x,x'} p^K_x(t)}{\int dF_K p^K_x(t)}
\] (11)
depends on all \( p^K \). However, this matrix will change if the distributions \( p^K_x(t) \) change, i.e., is not only a function of the state \( x \). Accordingly, it results in non-Markovian dynamics [22]. Note as well that \( \bar{K} = \int dF_K K \), the effective transition rate matrix, is not directly related to the dynamics of the effective probability distribution. In particular \( \bar{p}_x(t) \neq p^K_x(t) \) in general.

Next, write the effective internal energy as \( \mathbf{U} = \sum_p \tau_p \epsilon_p \). The first law of thermodynamics in terms of this effective internal energy can be expressed as \( \mathbf{U} = \mathbf{W} + \mathbf{Q} + \mathbf{W}_{\text{chem}} \). Similarly, we can introduce the effective entropy as \( \hat{S} = -\sum x p_x \ln p_x \) and write down the second law of thermodynamics as
\[
\hat{s} = \hat{s}_i + \hat{s}_e \] (12)
where
\[
\hat{s}_i = \int dF_K \hat{S}^K \geq 0
\] (13)
\[
\hat{s}_e = \int dF_K \hat{S}^K = \sum_{\nu} \beta^K \hat{Q}^{\nu,K}
\] (14)
(15)
(Note that we average over \( N \), and therefore over the number of terms in the sum in Eq. (15).) \( \hat{s}_i \) is the effective entropy production rate, and \( \hat{s}_e \) is the effective entropy flow rate.

Note that the effective entropy production is non-negative, as in conventional (no uncertainty) stochastic thermodynamics, since each \( \hat{S}^K \) is non-negative. However, there is no simple relation between the effective entropy flow rate and the effective heat flow rate, given by
\[
\hat{Q} = \sum_{\nu=1}^N \hat{Q}^{\nu,K}
\] (16)
(This discrepancy between the two rates would exist even if we knew with certainty that \( N = 1 \); it reflects the fact that there is statistical coupling between \( \beta^K \) and \( \hat{Q}^{\nu,K} \) when \( \beta^K \) is a random variable.) In particular, the derivative of the entropy is not necessarily lower-bounded by the heat flow rate, which means that this ensemble version of the second law of thermodynamics is not as consequential as the standard version.

We now turn our focus to trajectory-level thermodynamics. To begin, note that for a given trajectory \( x(t) \) and given energy spectrum, the stochastic energy does not depend on the transition rate matrix. Therefore stochastic work and stochastic total heat (heat plus chemical work) are independent of the rate matrix.

Next, define the effective stochastic entropy at time \( \tau \) as
\[
\mathbf{S}(x(\tau)) = -\log p_x(\tau)
\] (17)
Note that the effective stochastic entropy is not the same as the stochastic entropy of the effective distribution, \( -\log \bar{p}_x(t) \). If we average the trajectory-level decomposition of entropy, Eq. (6), over all possible transition rate matrices, we obtain
\[
\hat{s}(x(\tau)) = \hat{s}_i(x(\tau)) + \hat{s}_e(x(\tau))
\] (18)
where
\[
\hat{s}_i(x(\tau)) = \int dF_K \hat{s}^K_i(x(\tau)) = \sum_{\nu=1}^N \mathbb{P}_N \sum_{\nu=1}^N \beta^{\nu} \left( \epsilon^{\nu}(x(\tau)) - \mu^{\nu} n^{\nu}(x(\tau)) \right)
\] (19)
where in the last line we assume that \( \text{Cov}(\beta^{\nu}, \mu^{\nu}) = 0 \), i.e., that our uncertainty about the temperature is statistically independent of our uncertainty about the chemical potential.

By averaging Eq. (18) over all possible trajectories under the effective probability distribution \( \bar{p}_x(\tau) \), we obtain
\[
\langle \hat{s} \rangle = \langle \hat{s}_i \rangle + \langle \hat{s}_e \rangle
\] (20)
where we define \( \langle f(x(\tau)) \rangle := \sum_{x} f(x(\tau)) \bar{p}_x(\tau) \). Note that
\[
\langle \hat{s}_e \rangle_{p^K} \neq \langle \hat{s}_e \rangle_{\bar{p}} = \sum_{N=1}^N \mathbb{P}_N \sum_{\nu=1}^N \beta^{\nu} \hat{Q}^{\nu}
\] (21)
As shorthand, write the effective stochastic entropy as
\[
\mathbf{S} := \langle \hat{s} \rangle_{\bar{p}} = -\sum x \bar{p}_x \cdot \ln p_x
\] (22)
With help of Eq. (20) we can show that the effective stochastic entropy also satisfies the second law. In addition, the effective stochastic entropy exceeds the stochastic entropy, $\tilde{S}$:

$$\tilde{S} \geq \sum_{N=1}^{\infty} p_N \sum_{\nu=1}^{N} \beta^{\nu} Q^{\nu}. \quad (23)$$

**IV. SYSTEM COUPLED TO ONE RESERVOIR WITH SHARPLY PEAKED TEMPERATURE DISTRIBUTION**

In this section we consider the simple scenario where we are certain that the system is coupled to a single heat reservoir, i.e., $\theta = \bar{\beta}$ but are uncertain about the temperature of that reservoir. Via LDB, this uncertainty in temperature causes uncertainty in the rate matrix, and therefore uncertainty in the stochastic thermodynamics. For simplicity, we only consider the effect of this specific type of uncertainty on expectation values. We indicate such an effective value of a general thermodynamic variable $X(\bar{\beta})$ (possibly depending on the trajectory $x(t)$ defined in the time interval $[t_i, t_f]$) as

$$X = \int \mathrm{d}F_\beta X(\bar{\beta}) \quad (24)$$

To begin, we make a second-order expansion of $X$ in $\beta - \bar{\beta}$ to obtain

$$X \approx X(\bar{\beta}) + \frac{\beta \partial^2 X}{\partial \beta^2} |_{\bar{\beta}} \quad (25)$$

In particular, the effective heat flow to second order is

$$\bar{Q} \approx Q(\bar{\beta}) + \frac{\partial^2 Q}{\partial \beta^2}|_{\bar{\beta}} \quad (26)$$

Moreover, $\tilde{S}_e$ can be expanded as

$$\tilde{S}_e = \bar{\beta} Q = \int \mathrm{d}\beta p(\beta) \beta Q(\beta)$$

$$\approx \int \mathrm{d}\beta p(\beta) \left[ Q(\bar{\beta}) + (\beta - \bar{\beta}) \frac{\partial Q}{\partial \beta} |_{\bar{\beta}} + \frac{1}{2} (\beta - \bar{\beta})^2 \frac{\partial^2 Q}{\partial \beta^2} |_{\bar{\beta}} \right]$$

$$= \bar{\beta} Q(\bar{\beta}) + \frac{\partial Q}{\partial \beta} |_{\bar{\beta}} + \frac{1}{2} (\beta - \bar{\beta})^2 \frac{\partial^2 Q}{\partial \beta^2} |_{\bar{\beta}} \quad (27)$$

By plugging in for $Q(\bar{\beta})$ from Eq. (26), we obtain

$$\tilde{S}_e = \bar{\beta} Q + \frac{\partial Q}{\partial \beta} |_{\bar{\beta}} + \frac{1}{2} (\beta - \bar{\beta})^2 \frac{\partial^2 Q}{\partial \beta^2} |_{\bar{\beta}}$$

$$= \bar{\beta} Q - m_2(\beta) C_V + m_3(\beta) \left( C_V' + \frac{C_V''}{2\bar{\beta}} \right) \quad (28)$$

where $C_V = \frac{\partial^2 E}{\partial T^2}$ is the specific heat at $T = \frac{1}{\beta}$ and

$$m_k(\beta) = \frac{1}{\beta^k} - 1 \quad (29)$$

is the relative $k$-th moment. It is straightforward to show from Jensen’s inequality that $m_k(\beta) \geq 0$.

Note that for many cases the effective entropy flow is smaller than effective inverse temperature times effective heat. Consider, for example the case where $C_V = \text{const} > 0$, i.e., positive specific heat independent of temperature.) This can be interpreted as a violation of the second law for effective thermodynamic quantities. Formally, it arises because $\beta$ and $Q$ are statistically coupled, so $\bar{\beta} Q \neq \bar{\beta} \bar{Q}$. It is important to emphasize that this is not a physical violation of the second law. Experimentally, it would arise if we repeatedly prepare the system the same (imprecise) way, and interpret the resulting empirical average values of thermodynamic quantities as an average under one, fixed distribution, being repeatedly sampled in each experiment, when in fact the distribution itself varies from one experiment to the next.

We now use these preliminary results to investigate the trajectory thermodynamics when the distribution over temperature is highly peaked. First, we note that the effective change of entropy production $\Delta s_i$ across a trajectory $x(\tau)$ starting at $t_0$ and ending at $t_f$ can be expressed as

$$\Delta s_i = \ln \frac{\mathcal{P}^\beta(x(\tau))}{\mathcal{P}^\beta(\tilde{x}(\tau))} \quad (30)$$

where $\mathcal{P}^\beta$ is the probability of observing trajectory $x(\tau)$ for inverse temperature $\beta$, $\tilde{x}(\tau) = x(t_f - \tau)$ is the time-reversed trajectory $\tilde{P}$ is the probability for the time-reversed protocol $\tilde{\lambda}(x)$. We assume that for each $\beta$, we are certain about the initial and final distribution. By using expansion Eq. (25) we can express the effective entropy production change as:

$$\Delta s_i = \Delta s_i(\bar{\beta}) + \frac{\partial^2 \Delta s_i}{\partial \beta^2} |_{\bar{\beta}} \quad (31)$$

Furthermore, due to the fact that the trajectory entropy flow is a linear function of $\beta$, we can use the following identity:

$$\frac{\partial^2 \Delta s_i}{\partial \beta^2} \bigg|_{\beta = \bar{\beta}} = \frac{\partial^2 \Delta s}{\partial \beta^2} \bigg|_{\beta = \bar{\beta}} \quad (32)$$

An interesting special case is where the initial and final distribution are equilibrium distributions, as for example in Crooks’ theorem. So the equilibrium distribution for each $\beta$ is given by the Boltzmann distribution with corresponding temperature.

In this special case,

$$\frac{\partial^2 s}{\partial \beta^2} \bigg|_{\beta = \bar{\beta}} = \frac{\partial^2}{\partial \beta^2} (\beta \epsilon_x + \ln Z) \bigg|_{\beta = \bar{\beta}}$$

$$= \text{Var}(U)_{\bar{\beta}} = \sum_x \pi^\beta_x \epsilon^2_x - \left( \sum_x \pi^\beta_x \epsilon^2_x \right)^2 \quad (33)$$
so we finally obtain
\[ \Delta \bar{s}_i = \Delta s_i(\bar{\beta}) + \frac{1}{2} \text{Var}(\beta) \Delta \text{Var}(U)_{\bar{\beta}}. \]  
(34)

Depending on \( \Delta \text{Var}(U)_{\bar{\beta}} \), the trajectory entropy production can be smaller or bigger than for the case of effective temperature.

Expressing \( \Delta s_i(\bar{\beta}) \) from Eq. (31) and plugging it into the DFT for the entropy production change with effective temperature \( \ln \frac{P^\beta(x(t))}{P^\beta(\bar{x}(t))} = \Delta s_i(\bar{\beta}) \), it is possible to obtain the detailed fluctuation theorem for \( \bar{s}_i \) as

\[
P^\beta(\Delta s_i) = \int Dx(\tau) P^\beta(\bar{x}(\tau)) \delta \left( \Delta \bar{s}_i - \ln \frac{P^\beta(x(\tau))}{P^\beta(\bar{x}(\tau))} \right) = e^{\Delta s_i - \frac{1}{2} \text{Var}(\beta) \Delta \text{Var}(U)_{\bar{\beta}}} \bar{P}^\beta(-\Delta s_i) \]  
(35)

so we obtain
\[
\frac{P^\beta(\Delta s_i)}{P^\beta(-\Delta s_i)} = e^{\Delta s_i - \frac{1}{2} \text{Var}(\beta) \Delta \text{Var}(U)_{\bar{\beta}}}
\]  
(36)

Using this result to average over the ensemble of trajectories gives us the integrated fluctuation theorem

\[
\left\langle e^{\Delta s_i - \frac{1}{2} \text{Var}(\beta) \Delta \text{Var}(U)_{\bar{\beta}}} \right\rangle_{P^\beta} = 1
\]  
(37)

By using Jensen inequality, we finally obtain
\[
\langle \Delta \bar{s}_i \rangle_{\bar{\beta}} \geq \frac{1}{2} \text{Var}(\beta) \Delta \text{Var}(U)_{\bar{\beta}}
\]  
(38)

So depending on whether \( \Delta \text{Var}(U)_{\bar{\beta}} \) is positive or negative (i.e., whether the internal energy variance is increased or decreased during the experiment), the effective entropy production will be positive or negative.

Finally, by plugging \( \Delta s_i(\bar{\beta}) = \bar{\beta}(w - \Delta F(\bar{\beta})) \) into Eq. (34) (where \( F(\bar{\beta}) \) is the equilibrium free energy for temperature \( \bar{\beta} \)), we obtain
\[
\Delta \bar{s}_i = \bar{\beta}(w - \Delta F(\bar{\beta})) + \frac{1}{2} \text{Var}(\beta) \Delta \text{Var}(U)_{\bar{\beta}}.
\]  
(39)

By taking the ensemble average under the effective probability distribution, we obtain
\[
\bar{W} \geq \Delta \bar{F} + \frac{1}{2} \text{Var}(\beta) \Delta \text{Var}(U)_{\bar{\beta}}.
\]  
(40)

Next, we can expand the effective equilibrium free energy as
\[
\bar{F} = F(\bar{\beta}) + \frac{1}{2} \text{Var}(\beta) \frac{\partial^2 F}{\partial \beta^2} |_{\bar{\beta}}
\]  
(41)

where
\[
\frac{\partial^2 F}{\partial \beta^2} |_{\bar{\beta}} = \frac{\partial^2}{\partial \beta^2} \left( -\frac{1}{\beta} \ln Z(\beta) \right) |_{\bar{\beta}}
\]
\[
= \frac{2 F(\bar{\beta})}{\beta^2} - \frac{2 U(\bar{\beta})}{\beta^2} - \frac{\text{Var}(U)_{\bar{\beta}}}{\beta}
\]  
(42)

V. OPTIMAL WORK EXTRACTION FROM A SYSTEM WITH UNCERTAIN TEMPERATURE

In this and the following section we consider the foundational issue of the minimal thermodynamic costs necessary to evolve an (uncertain) initial distribution to a (perfectly known) desired final distribution, by appropriate choice of a (perfectly known) time-dependent Hamiltonian. For simplicity, we also assume in both sections that we know with certainty that there is only one reservoir during the system’s evolution, and there are no particle interchanges between the system and that reservoir during that evolution. (So the reservoir is a heat bath.)

While we can impose an arbitrary time-dependent Hamiltonian \( H_t(x) \) on the system, since we assume that the system obeys LDB at all times with respect to that Hamiltonian, the rate matrix at any given moment will depend on the temperature. For completeness, we assume that we have zero uncertainty about this dependence, i.e., there is a single-value function mapping \( (H_t(x), \beta) \rightarrow K_{x,x}(t) \) which we can set arbitrarily (subject to the constraint of LDB), and which we know with zero uncertainty. Accordingly, our choice of \( H_t \) would determine the full function \( K_{x,x}(t) \) with zero uncertainty, if it weren’t for uncertainty about the temperature.

We start in this section by considering the case where in addition to being uncertain about the initial distribution, we are also uncertain about the temperature of the heat reservoir coupled to the system during its evolution. We further suppose that the (uncertain) initial distribution is specified by the temperature of the heat reservoir that will govern the system’s evolution from that distribution. However, we allow this specification to be flexi-
ble; we do not require that the initial distribution be an equilibrium for the heat reservoir.

Formally, in this section we suppose that we have an initial set of distributions, one for each allowed temperature \( \beta \), written as \( p_x(t_i|\beta) \). As mentioned above, we do not assume that each of those distributions is at equilibrium for the associated temperature. Physically, we imagine a set of different physical apparatuses, each connected to its own reservoir with (inverse) temperature \( \beta \), and each with its own distribution, \( p_x(t_i|\beta) \), where we randomly pick one of those apparatuses, without knowing which one we have picked, by randomly sampling a distribution \( d\beta = f(\beta) d\beta \). Write the associated \( \beta \)-averaged initial distribution over \( x \) as

\[
\bar{p}_x(t_i) = \frac{\sum_{\beta} f(\beta) p_x(t_i|\beta)}{\sum_{\beta} f(\beta) Z(\beta)}
\]

(44)

After choosing one of the apparatuses this way, we apply some protocol, ending with some effective distribution

\[
\bar{p}_x(t_f) = \frac{\sum_{\beta} f(\beta) p_x(t_f|\beta)}{\sum_{\beta} f(\beta) Z(\beta)}
\]

(45)

We also have a target ending distribution, \( p^*_{x,\beta} \), and want to evolve \( \bar{p}_x(t_i) \) to that target distribution. We are interested in minimizing the (dissipated) work required to do this. To simplify the analysis, we assume that there is one and only one Hamiltonian \( H^*_t(x) \) such that the target distribution is a \( \beta \)-average of the associated equilibrium distribution for Hamiltonian \( H^*_t(x) \), i.e.,

\[
p^*_x = \frac{\sum_{\beta} f(\beta) e^{-\beta H^*_t(x)}}{\sum_{\beta} f(\beta) e^{-\beta H^*_t(x)}}
\]

(46)

\[
\sum_{\beta} f(\beta) e^{-\beta H^*_t(x)}
\]

(47)

If the protocol changes \( p_x(t_i) \) to \( p^*_x \) in finite time, then in general it will not end with each distribution \( p_x(t_f|\beta) \) equal to the associated Boltzmann distribution. (So if we were to watch the system evolve after the ending time \( t = 1 \), we would see it change from \( p^* \).) Even if the protocol takes infinite time though, in general there will be more than one protocol that sends the initial distribution \( p_x(t_i) \) to \( p^*_x(t_f) = \bar{p}_x(t_f) \). Whatever the protocol is, for each \( \beta \) there will be an associated amount of EP that would arise if that apparatus were the one chosen in our initial sampling process. The \( \beta \)-average of those EPs is the \( \beta \)-average of the potentially extractable work that will be dissipated due to our not being able to tailor the protocol to match the actual apparatus and its inverse temperature \( \beta \). Our goal is to find which protocol generates minimal \( \beta \)-averaged EP while ending with the target distribution.

In this section we restrict attention to a protocol that comprises a conventional \{quench; equilibrate; semistatically-evolve\} process \[9, 15\]. Note that in the intermediate step, after the initial quench, we wait an arbitrarily long time, to allow the system to thermalize for the new (post-quench) Hamiltonian, for whatever \( \beta \) the system happens to have. So whatever semi-static evolution the system undergoes after that step, it will generate no EP, i.e., all of the \( \beta \)-averaged EP is generated in the thermalization step.

Define \( H^*_t(x) \) as the post-quench Hamiltonian that minimizes that \( \beta \)-averaged EP. To solve for \( H^*_t(x) \), first note that for each \( \beta \), the EP generated as \( P_x(t_i|\beta) \) relaxes to the associated equilibrium is given the Kullback Liebler divergence between two distributions over \( X \):

\[
D \left( p_X(t_i|\beta) \bigg|\bigg| \frac{e^{-\beta H^*_t(X)}}{Z(H^*_t, \beta)} \right) = \sum_{x} f(\beta) \left[ \beta p_x(t_i|\beta) - e^{-\beta H^*_t(x)}/Z(H^*_t, \beta) \right] + \ln Z(H^*_t, \beta)
\]

(48)

The \( \beta \)-averaged EP is the \( \beta \)-average of this KL divergence. Since the \( \beta \)-averaged entropy of \( p_x(t_i|\beta) \) is independent of \( H^*_t(x) \), this means that \( H^*_t(x) \) is the minimizer of

\[
\sum_{\beta} f(\beta) \left[ \sum_x p_x(t_i|\beta) \beta H^*_t(x) + \ln Z(H^*_t, \beta) \right]
\]

(49)

Differentiating Eq. (63) with respect to \( H^*_t(x) \) for each \( x \) gives a set of coupled equations, one for each \( x \):

\[
\sum_{\beta} f(\beta) \beta p_x(t_i|\beta) - e^{-\beta H^*_t(x)}/\sum_{x'} e^{-\beta H^*_t(x')} = 0
\]

(50)

or if we define \( g(x) := \sum_{\beta} f(\beta) \beta p_x(t_i|\beta) \),

\[
g(x) = \sum_{\beta} f(\beta) e^{-\beta H^*_t(x)}/\sum_{x'} e^{-\beta H^*_t(x')}
\]

(51)

(Compare to Eq. (47).)

The effective reversible work expended during the semi-static evolution is the change in equilibrium (!) free energy during the semi-static evolution,

\[
W^{ss} := \sum_{\beta} f(\beta) \left[ F_\beta(H^*_t) - F_\beta(H^*_t) \right]
\]

(52)

\[
= \sum_{\beta} f(\beta) \beta^{-1} \left[ \ln Z(\beta, H^*_t) - \ln Z(\beta, H^*_t) \right]
\]

(53)

The associated change in effective energy is

\[
\Delta E^{ss} := \sum_{\beta, x} f(\beta) \left[ H^*_t(x) - H^*_t(x) \right] e^{-\beta H^*_t(x)}/Z(H^*_t, \beta) - H^*_t(x) e^{-\beta H^*_t(x)}/Z(H^*_t, \beta)
\]

(54)

The difference of those is the total heat during the semi-static evolution, \( Q^{ss} \). If we plug the optimal \( H^*_t(x) \) solving Eq. (51) into Eq. (48), we get a formula for the \( \beta \)-averaged dissipated
work during the full protocol, $W_{\text{diss}}$. In addition, if we write the initial, pre-quench Hamiltonian as $H_{t_i}(x)$, then the work during the quench is
\[
W^q := \sum_{\beta, x} f(\beta) p_x(t_i | \beta) \left[ H_{t_i}^*(x) - H_{t_i}(x) \right] \tag{55}
\]
(In general, the dissipated work during the full protocol will differ from the actual work, since the change in entropy as the system relaxes to its equilibrium distribution is work that could have been extracted but wasn’t.)

If we add $W^q$ to $W^{ss}$, we get the total reversible work during the full protocol. Now adding the $\beta$-averaged dissipated work gives the total work during the full protocol,
\[
W^f = W^{ss} + W^q + W_{\text{diss}} \tag{56}
\]
which provides a bound to the question motivating our analysis, of how much work can be extracted. (The reason this is only a bound is that we have not proven that in the scenario considered here, the \{quench; equilibrate; semistatically-evolve\} process is optimal.)

In addition, the total change in internal energy during the full protocol is
\[
\Delta E^f := \Delta E^{ss} + W^q
\]
\[
+ \sum_{\beta, x} f(\beta) H_{t_i}(x) \left[ e^{-\beta H_{t_i}(x)} - p_x(t_i | \beta) \right] \tag{57}
\]
\[
= W^q + \sum_{\beta, x} f(\beta) \left[ H_{t_i}^*(x) e^{-\beta H_{t_i}^*(x)} Z(H_{t_i}^*, \beta) - p_x(t_i | \beta) \right] \tag{58}
\]
Now recall that in conventional, equilibrium thermodynamics, if we move a system isothermally and semistatically from one equilibrium to another, the difference between the work expended and the change in internal energy is the change in entropy (up to a multiplicative factor given by the temperature). We would like an analogous interpretation to hold here. That means we want to be able to interpret the difference $W^f - \Delta E^f$ as the change in a generalized entropy during the full protocol, i.e., we want there to be some functional $S^f$ such that we can write
\[
S^f(p(t_i)) - S^f(p^*) = W_{\text{diss}} + W^{ss} - \sum_{\beta, x} f(\beta) \left[ H_{t_i}^*(x) e^{-\beta H_{t_i}^*(x)} Z(H_{t_i}^*, \beta) - p_x(t_i | \beta) \right] \tag{59}
\]

VI. DYNAMICS OF THE THERMODYNAMIC VALUE OF INFORMATION

We now investigate a more controlled version of the scenario considered in the previous section. Just like in the previous section, here we are uncertain about the initial distribution. However, in contrast to the scenario considered in the previous section, here we are certain that the system evolves while coupled to a (single) heat reservoir with temperature $\beta = 1$. To emphasize this distinction, here we index the initial set of distributions by an uncertain parameter $\alpha$ (not necessarily equal to a temperature), writing it as $p_x(t_i | \alpha)$. So the $\alpha$-averaged distribution over $x$ is
\[
p_x(t_i) = \sum_{\alpha} f(\alpha) p_x(t_i | \alpha) \tag{60}
\]
Physically, we imagine a process where we first randomly sample $f(\alpha)$, choosing one of the distributions, but don’t know which one was chosen. As in the previous section, we want to apply a standard \{quench; equilibrate; semistatically-evolve\} process to that system, in order to change the (unknown) distribution $p_x(t_i | \alpha)$, whatever it is, to the (perfectly known) desired ending distribution $p_x(t_f) = P_x$ no matter what $\alpha$ is. However, in contrast to the analysis of the previous section, here we consider the case where the evolution takes place while the system is coupled to some single fixed heat reservoir at temperature $k_B T = 1$, no matter what $\alpha$ is. In addition, we assume that there is a (perfectly known) delay between when the initial distribution is generated and when the \{quench; equilibrate; semistatically-evolve\} process begins, during which time the system evolves according to a known rate matrix.

Our ultimate interest is in how the length of that delay affects the EP. To begin with, we consider the simplest case where the delay is zero, i.e., the \{quench; equilibrate; semistatically-evolve\} process begins immediately after the initial distribution is randomly generated. First, note that if the distributions $p_x(t_i | \alpha)$ are not all the same, there is no single Hamiltonian $H(x)$ we can quench to so that every $p_x(t_i | \alpha)$ (one for each $\alpha$) is at equilibrium for that $H(x)$. So as in the previous section, whatever $H(x)$ we quench to will mean that the equilibrium step, before the semistatic evolution, will result in a nonzero $\alpha$-average of the (conventionally defined) EP of each of the separate distributions $p_x(t_i | \alpha)$ as that distribution relaxes to the equilibrium distribution defined by $H(x)$ and that $\alpha$. So all the EP arises while the system is equilibrating.

Define $H(t_i)(x)$ as the Hamiltonian that minimizes the $\alpha$-average of this initial EP. To solve for $H(t_i)$, first note that for each $\alpha$, whatever Hamiltonian $H$ we use, the EP generated as $p_x(t_i | \alpha)$ relaxes to equilibrium is
\[
D \left( p_x(t_i | \alpha) \right) \mid \left( e^{-H(x)} / Z(H) \right) \tag{61}
\]
where as usual the partition function is
\[
Z(H) := \sum_x e^{-H(x)} \tag{62}
\]
The $\alpha$-averaged EP is the $\alpha$-average of this KL divergence. Since the $\alpha$-averaged entropy of $P_t(\alpha)$ is independent of $H(x)$, $H^\alpha_t(x)$ is the minimizer of

$$\sum_x p_x(t_i) \left[ H(x) + \ln Z(H) \right] = \ln Z(H) + \sum_x p_x(t_i) H(x)$$

(63)

where

$$p_x(t_i) := \sum_\alpha f(\alpha)p_x(t_i|\alpha)$$

(64)

Differentiating Eq. (63) with respect to $H(x)$ for each $x$ gives

$$p_x(t_i) = \frac{e^{-H(x)}}{\sum_{x'} e^{-H(x')}}$$

(65)

So

$$H^\alpha_t(x) = -\ln P_x(t_i)$$

(66)

Note that this is the exact result one would have derived if one had simply marginalized over the uncertainty about the initial distribution and then applied the conventional calculation of what quenched Hamiltonian results in minimal EP.

Write $S(P_t(X|\alpha))$ for the conditional entropy of $X$ given $\alpha$ under joint distribution $P_t(X, \alpha) = f(\alpha)p_t(X|\alpha)$. Then we can write the EP — all generated in the stage where the system equilibrates — as

$$\sum_\alpha P(\alpha) D \left( P_t(X|\alpha) \parallel \frac{e^{-H^\alpha_t(x)}}{Z(H^\alpha_t)} \right)$$

$$= \langle H^\alpha_t \rangle_{P_t} - S(P_t(X|\alpha)) + \ln Z(H^\alpha_t)$$

(67)

$$= S(P_t(X)) - S(P_t(X|\alpha))$$

(68)

$$= I_{P_t}(X; \alpha)$$

(69)

which is just the Jensen Shannon divergence of the set of distributions $\{P(x|\alpha)\}$, weighted according to $P(\alpha)$.

This Jensen Shannon divergence is just the usual expression for the “thermodynamic value of information”, i.e., for the amount that the minimal extractable work changes if we can measure some statistic $\alpha$ concerning the initial distribution of the state of the system compared to how much we can extract if we can’t measure that statistic.

As a variation of the scenario considered above, suppose that we are delayed in when we can start the quench process, until some time $\tau > 0$ after $P(\alpha)$ is sampled. In other words, suppose that after $\alpha$ is randomly chosen, but before the quench process starts, the system evolves according to a known rate matrix, $W^{x'}_{x}(t)$, that is the same for all $\alpha$, up to some time $\tau$, when the quench process starts. If we take the time-derivative of this value of information with respect to $\tau$ we get

$$\frac{dI_{P_t}(X; \alpha)}{d\tau} = \frac{dS(P_t(X))}{d\tau} - \frac{dS(P_t(X|\alpha))}{d\tau}$$

$$\equiv \sum_\alpha P(\alpha) \sum_{x,x'} W^{x'}_{x}(\tau)P_t(x'|\alpha) \ln \frac{\sum_\alpha P(\alpha')W^{x'}_{x}(\tau)P_t(x'|\alpha')}{\sum_\alpha P(\alpha')W^{x'}_{x}(\tau)P_t(x|\alpha')} - \ln \frac{W^{x'}_{x}(\tau)P_t(x|\alpha)}{W^{x'}_{x}(\tau)P_t(x|\alpha)}$$

(70)

This difference in derivatives of entropies equals the difference between two EP rates, distinguished by whether we know $\alpha$ or not; the EF rate doesn’t depend on our knowledge about $\alpha$, and so the two EP rates (one for knowing $\alpha$, one for averaging over $\alpha$) cancel.

In addition, if we multiply and divide by $P(\alpha)$ inside the rightmost logarithm in Eq. (71), and then apply the log-sum inequality, we see that $I_{P_t}(X; \alpha)$ is monotonically increasing in time. (We can derive the same

$$\equiv \sum_\alpha P(\alpha) \sum_{x,x'} W^{x'}_{x}(\alpha,\tau)P_t(x'|\alpha) \ln \frac{\sum_\alpha P(\alpha')W^{x'}_{x}(\alpha',\tau)P_t(x'|\alpha')}{\sum_\alpha P(\alpha')W^{x'}_{x}(\alpha',\tau)P_t(x|\alpha')} - \ln \frac{W^{x'}_{x}(\alpha,\tau)P_t(x|\alpha)}{W^{x'}_{x}(\alpha,\tau)P_t(x|\alpha)}$$

(72)

result with the data-processing inequality.) Physically, this means that the minimal dissipated work that would arise if we used our \{quench; equilibrate; semistatically-evolve\} process grows the longer we wait to use it, assuming the system is undergoing $\alpha$-independent dynamics.

Next, suppose that $\alpha$ indexes not just the distribution, but also the rate matrix, i.e., suppose that we are unsure about the dynamics as well as the distribution. Then we must write $W^{x'}_{x}(\alpha, \tau)$ instead of $W^{x'}_{x}(\tau)$, and the dynamics of the value of information becomes

$$\frac{dI_{P_t}(X; \alpha)}{d\tau} = \sum_\alpha P(\alpha) \sum_{x,x'} W^{x'}_{x}(\alpha,\tau)P_t(x'|\alpha) \ln \frac{\sum_\alpha P(\alpha')W^{x'}_{x}(\alpha',\tau)P_t(x'|\alpha')}{\sum_\alpha P(\alpha')W^{x'}_{x}(\alpha',\tau)P_t(x|\alpha')} - \ln \frac{W^{x'}_{x}(\alpha,\tau)P_t(x|\alpha)}{W^{x'}_{x}(\alpha,\tau)P_t(x|\alpha)}$$

(73)

Now the data-processing inequality doesn’t apply. However, we can still use the log-sum inequality, to again
conclude that $I_{P_i}(X;\alpha)$ is monotonically increasing in time.

A natural question is whether adding uncertainty to the rate matrix can cause the rate of increase in time of $I_{P_i}(X;\alpha)$ to shrink, e.g., formalized as whether the following quantity can be negative:

$$\sum_{\alpha} P(\alpha) \sum_{x,x'} \left[ W^{\tau}_{x} (\alpha, \tau) P_{\tau}(x'|\alpha) \ln \frac{\sum_{\alpha'} P(\alpha') W^{\tau}_{x} (\alpha', \tau) P_{\tau}(x'|\alpha')}{\sum_{\alpha'} P(\alpha') W^{\tau}_{x} (\alpha', \tau) P_{\tau}(x|\alpha')} - W^{\tau}_{x} (\tau) P_{\tau}(x'|\alpha) \ln \frac{\sum_{\alpha'} P(\alpha') W^{\tau}_{x} (\tau) P_{\tau}(x'|\alpha')}{\sum_{\alpha'} P(\alpha') W^{\tau}_{x} (\tau) P_{\tau}(x|\alpha')} \right]$$

(73)

where $W^{\tau}_{x} (\tau) := \sum_{\alpha''} P(\alpha'') W^{\tau}_{x} (\alpha'', \tau)$. In the special case where all distributions $P(x|\alpha)$ are the same, so that the only uncertainty is in the rate matrix, the expression in Eq. (73) equals 0. Nonetheless, by applying the log-sum inequality to Eq. (72) for $P_i(x|\alpha)$ independent of $\alpha$ we see that the rate of increase of the value of information is still non-negative, even when our only uncertainty concerns the rate matrix.

**VII. DISCUSSION AND FUTURE WORK**

In any real-world experimental test of a system there are three major types of uncertainty: Uncertainty about the state of the system; uncertainty about the state of the external environment that the system is interacting with; uncertainty about the parameters of the equations governing the dynamics of the system and its interaction with its external environment. In (classical) stochastic thermodynamics, the first type of uncertainty is addressed by replacing specification of the system’s state, and the second one is typically addressed by assuming the environment is infinite, at equilibrium, and evolving far faster than does the system (“separation of time scales”). In essence, the entire field of stochastic thermodynamics concerns the consequences of those two types of uncertainty for the dynamics of energy and particle counts in the system. However, very little attention (if any) has been paid so far to the third type of uncertainty. Here we begin an investigation of the consequences of that third type of uncertainty, showing that it entails major modifications to the standard results previously derived in stochastic thermodynamics.

Our investigations have only scratched the surface of issues involved with this third type of uncertainty. Some of the more immediate questions to be addressed in future work include:

1. For pedagogical simplicity we did not explicitly model uncertainty in the energy spectrum and / or associated dynamics of the rate matrix in the analysis in Section III. Future work involves analyzing the relationship between the thermodynamic consequences of those uncertainties and the thermodynamic consequences of the uncertainties that we did explicitly consider in Section III.

2. How does the analysis in Section IV change if we include low-order expansions of other parameters besides temperature?

3. The approach outlined in Section V defines generalized entropy using the total work expended during the \{quench; equilibrate; semistatically-evolve\} process that takes $(P_i(x), H_i^{-}(x)) \rightarrow (P^*(x), H_i^{-}(x))$ with minimal dissipated work. Is that process the same as the one that minimizes the total work during any (quench-thermalize-evolve) process that takes $(P_i(x), H_i^{-}(x)) \rightarrow (P^*(x), H_i^{+}(x))$?

4. Is there any alternative protocol which, like the \{quench; equilibrate; semistatically-evolve\} process discussed above is ignorant of $\beta$, and which also maps $P_i(x) \rightarrow P^*(x)$ in infinite time, but has less $\beta$-averaged EP than the quench-thermalize-evolve protocol?

5. Is there any such process which finishes in finite time, so that $P_i(x|\beta)$ is not an equilibrium distribution for $H_i(x)$ for all $\beta$?

6. Is there any alternative protocol to the \{quench; equilibrate; semistatically-evolve\} process considered in Section VI which is also ignorant of $\alpha$, and which also maps each possible initial distribution $P_i(x|\alpha)$ to $P_i(x)$, but has less $\alpha$-averaged EP than $I_{P_i}(X;\alpha)$?

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[1] C. Beck and E.G.D. Cohen, *Superstatistics*, Physica A 322 (2003), 267–275.

[2] Gili Bisker, Matteo Polettini, Todd R Gingrich, and Jordan M Horowitz, *Hierarchical bounds on entropy produc-
tion inferred from partial information, Journal of Statistical Mechanics: Theory and Experiment 2017 (2017), no. 9, 093210.

Sergio Davis and Gonzalo Gutiérrez, Temperature is not an observable in superstatistics, Physica A: Statistical Mechanics and its Applications 505 (2018), 864–870.

Massimiliano Esposito, Katja Lindenberg, and Christian Van den Broeck, Entropy production as correlation between system and reservoir, New Journal of Physics 12 (2010), no. 1, 013013.

Massimiliano Esposito and Christian Van den Broeck, Three faces of the second law. i. master equation formulation, Physical Review E 82 (2010), no. 1, 011143.

Carlos E. Fiore and Mário J. de Oliveira, Entropy production and heat capacity of systems under time-dependent oscillating temperature, Phys. Rev. E 99 (2019), 052131.

Vladimir García-Morales and Katharina Krischer, Superstatistics in nanoscale electrochemical systems, Proceedings of the National Academy of Sciences 108 (2011), no. 49, 19535–19539.

Rudolf Hanel, Stefan Thurner, and Murray Gell-Mann, Generalized entropies and the transformation group of superstatistics, Proceedings of the National Academy of Sciences 108 (2011), no. 16, 6390–6394.

H-H Basegawa, J Ishikawa, K Takeo, and DJ Driebe, Generalization of the second law for a nonequilibrium initial state, Physics Letters A 374 (2010), no. 8, 1001–1004.

R. Kawai, J. M. R. Parrondo, and Christian Van den Broeck, Dissipation: the phase-space perspective, Physical Review Letters 98 (2007), no. 8, 080602.

Miki Matsuo and Shin ichi Sasa, Stochastic energetics of non-uniform temperature systems, Physica A 276 (2000), no. 1, 188–200.

We note though there is a substantial literature in which adopts an “inclusive Hamiltonian” framework, in which the external environment is finite, and the joint dynamics of the system-environment is explicitly modeled. This has been explored either with explicit Hamiltonian dynamics, with only randomness in the initial state [4, 10, 16] or at least approximate Hamiltonian dynamics [19, 21, 23, 24].

We note though that it is already known that if we do not account for all thermodynamic reservoirs, we invariably undercount the total of entropy production in a process [5].

Uncertainty in the energy spectrum and / or the time-dependence of the rate matrix can also be included in the analysis, at the cost of more complex notation.

Juan MR Parrondo, Jordan M Horowitz, and Takahiro Sagawa, Thermodynamics of information, Nature Physics 11 (2015), no. 2, 131–139.

Krzysztof Ptaszynski, First-passage times in renewal and nonrenewal systems, Physical Review E 97 (2018), no. 1, 012127.

Fábio Sattin, Bayesian approach to superstatistics, The European Physical Journal B-Condensed Matter and Complex Systems 49 (2006), no. 2, 219–224.

Udo Seifert, Stochastic thermodynamics, fluctuation theorems and molecular machines, Reports on Progress in Physics 75 (2012), no. 12, 126001.

First and second law of thermodynamics at strong coupling, Physical Review Letters 116 (2016), no. 2, 020601.
Appendix A: Brief review of stochastic thermodynamics

\[ \dot{p}_x(t) = \sum_{x'} K_{x,x'} p_{x'}(t) = \sum_{x'} J_{x,x'} . \]  

(A1)

Transition rates can be decomposed as

\[ K_{x,x'} = \sum_{\nu=1}^{N} K_{x,x'}^\nu . \]  

(A2)

The local equilibrium distribution is defined as

\[ \pi_x^\nu = \frac{\exp(-\beta_v(\epsilon_x - \mu_v n_x))}{Z^\nu} . \]  

(A3)

Transition rates fulfill local detailed balance, so

\[ \frac{K_{x,x'}^\nu}{K_{x',x}^\nu} = \frac{\pi_x^\nu}{\pi_{x'}^\nu} = e^{-\beta_v[(\epsilon_x - \epsilon_{x'}) - \mu_v(n_x - n_{x'})]} . \]  

(A4)

Thus, local flows

\[ J_{x,x'}^\nu = K_{x,x'}^\nu p_{x'}(t) - K_{x',x}^\nu p_x(t) \]  

(A5)

vanish for local equilibrium distributions.

We define internal energy of the system as

\[ U = \sum_x p_x \epsilon_x . \]  

(A6)

The first law of thermodynamics can be formulated as follows:

\[ \dot{U} = \dot{W} + \dot{Q} + \dot{W}_{chem} \]  

(A7)

where

\[ \dot{W} = \sum_x p_x \dot{\epsilon}_x \]  

(A8)

\[ \dot{Q} = \sum_{\nu} \dot{Q}^\nu = \sum_{\nu} \sum_x \dot{p}_x (\epsilon_x - \mu_v n_x) \]  

(A9)

\[ \dot{W}_{chem} = \sum_{\nu} \dot{W}_{chem}^\nu = \sum_{\nu} \sum_x \dot{p}_x \mu_v n_x \]  

(A10)

Entropy of the system is defined as

\[ S = -\sum_x p_x \ln p_x \]  

(A11)

Second law of thermodynamics can be expressed as follows:

\[ \dot{S} = \dot{S}_i + \dot{S}_e \]  

(A12)

where

\[ \dot{S}_i = \frac{1}{2} \sum_{x,x',\nu} J_{x,x'}^\nu \ln \frac{W_{x,x'}^\nu p_x}{K_{x,x'}^\nu p_{x'}} \geq 0 \]  

(A13)

\[ \dot{S}_e = \frac{1}{2} \sum_{x,x',\nu} J_{x,x'}^\nu \ln \frac{W_{x,x'}^\nu}{K_{x,x'}^\nu} \]  

(A14)

**Trajectory thermodynamics and fluctuation theorems:**

We consider a stochastic trajectory \( x(\tau) \). We define stochastic energy as \( \epsilon(\tau) = \epsilon_x(\tau) \). We also consider that particle levels \( n_x \) are independent of time. The first law of thermodynamics can be expressed on the trajectory level as

\[ \frac{d}{dt} \epsilon(\tau) = \dot{w}(\tau) + \dot{q}(\tau) + \dot{w}_{chem}(\tau) \]  

(A15)

where

\[ \dot{w} = \sum_x \delta_{x,x}(\tau) \dot{\epsilon}_x(\tau) \]  

(A16)

\[ \dot{q} + \dot{w}_{chem}(\tau) = \sum_x \delta_{x,x}(\tau) \dot{\epsilon}_x(\tau) \]  

(A17)

It is important to stress that the first law of thermodynamics is the pure energetic balance which does depends neither on the number of reservoirs nor on their parameters. Heat and chemical work can be decomposed into contributions from particular reservoirs

\[ \dot{q} = \sum_{\nu} \dot{q}^\nu(\tau) = \sum_{\nu} \delta_{x,x}(\tau) (\epsilon_x(\tau) - \mu_v n_x(\tau)) \]  

(A18)

\[ \dot{w}_{chem} = \sum_{\nu} \dot{w}_{chem}^\nu(\tau) = \sum_{\nu} \delta_{x,x}(\tau) H_x n_x(\tau) \]  

(A19)

Stochastic entropy along a trajectory \( x(\tau) \) can be defined as

\[ s_x(\tau) = -\ln p_x(\tau) . \]  

(A20)

It is straightforward to show that stochastic entropy fulfills the second law of thermodynamics, i.e.,

\[ \dot{s} = \dot{s}_i + \dot{s}_e \]  

(A21)

where

\[ \dot{s}_e = \sum_{\nu} \beta_v \dot{q}^\nu \]  

(A22)

By averaging over the trajectory ensemble, we obtain the ensemble second law of thermodynamics in the form \( \langle s_i \rangle = \dot{S}_i \geq 0 \).

Stochastic entropy production satisfies the well-known fluctuation theorem, which is a consequence of the following expression:

\[ \ln \frac{P_x(\tau)}{P_{\hat{x}}(\tau)} = \Delta s_i \]  

(A23)

where \( P_x(\tau) \) is the probability of stochastic trajectory \( x(\tau) \) for a protocol \( \lambda(\tau) \) and \( P_{\hat{x}}(\tau) \) is the probability of observing time-reversed trajectory \( \hat{x}(\tau) = x(T - \tau) \) for a time-reversed protocol \( \hat{\lambda}(\tau) = \lambda(T - \tau) \). It is straightforward to show that \( \Delta s_i \) obeys the detailed fluctuation theorem (DFT)

\[ \frac{P(\Delta s_i)}{P(-\Delta s_i)} = e^{\Delta s_i} \]  

(A24)

as well as integrated fluctuation theorem (IFT)

\[ \langle e^{-\Delta s_i} \rangle = 1 . \]  

(A25)
Appendix B: General form of transition matrix satisfying local detailed balance

We now focus on the most general form of transition matrix which fulfills local detailed balance. We denote transition rate matrix as \( K = \{ K_{x,x'} \}_{x,x'} \) and probability distribution \( p(t) = \{ p_x(t) \}_x \). We start with the most general form of a transition matrix satisfying detailed balance, which is a special case of local detailed balance when a system is coupled to one reservoir. We define the equilibrium distribution \( \pi = \{ \pi_x \}_x \) as the solution of

\[
K \pi = 0. \tag{B1}
\]

We define \( \Pi = \text{diag}(\pi) \) where \( \text{diag} \) denotes a diagonal matrix with diagonal elements equal to elements of the vector. Requirement of detailed balance from Eq. (A4) can be in the matrix notation rewritten as

\[
K \Pi = (K \Pi)^T \tag{B2}
\]

We consider the following decomposition of the transition rate matrix:

\[
K = R \Pi^{-1} \tag{B3}
\]

Then, we obtain from Eq. (B2) that \( R = R^T \), i.e., the matrix is symmetric. It is actually possible to show that Eq. (B4) is the most general decomposition of the transition rate matrix satisfying detailed balance. The normalization of the transition rate matrix is obtained in the diagonal elements of \( R \). For a general matrix \( R' \), the general transition rate matrix can be expressed as

\[
K = R' \Pi^{-1} - \text{diag} (R' \Pi^{-1} \cdot 1) \tag{B4}
\]

where \( \cdot \) denotes standard application of matrix to a vector and \( 1 = (1, \ldots, 1) \). In the following, we always assume that the matrix \( R \) is chosen so that \( K \) is normalized \((\sum_x K_{x,x'} = 0)\). Consequently, the probability flow can be expressed as follows:

\[
J_{x,x'} = R_{x,x'} \left( \frac{p_{x'}(t)}{\pi_{x'}} - \frac{p_x(t)}{\pi_x} \right) \tag{B5}
\]

from which we immediately see that the system satisfies detailed balance. A matrix satisfying local detailed balance (LDB-obeying matrix) is then a sum of matrices satisfying detailed balance, so

\[
K = \sum_{\nu} K_{\nu} = \sum_{\nu=1}^N R_{\nu} (\Pi_{\nu})^{-1} \tag{B6}
\]

We now assume the local equilibrium distribution in the form of Boltzmann distribution. Then, \( \Pi_{\nu} \) is parameterized by \( \alpha_{\nu} = (\beta_{\nu}, \mu_{\nu}) \) (we consider that the energy levels are known and fixed). We also denote \( R = \{ R_{\nu} \}_{\nu=1}^N \), then a general transition matrix satisfying local detailed balance can be characterized by the following variables

\[
K(N; \theta, R) = \sum_{\nu=1}^N R_{\nu} (\Pi_{\nu})^{-1} - \text{diag} \left( R_{\nu} (\Pi_{\nu})^{-1} \cdot 1 \right) \tag{B7}
\]