General linear thermodynamics for periodically driven systems with multiple reservoirs

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We derive a linear thermodynamics theory for general Markov dynamics with both steady-state and time-periodic drivings. Expressions for thermodynamic quantities, such as chemical work, heat, and entropy production are obtained in terms of equilibrium probability distribution and the drivings. The entropy production is derived as a bilinear function of thermodynamic forces and the associated fluxes. We derive explicit formulae for the Onsager coefficients and use them to verify the Onsager-Casimir reciprocal relations. Our results are illustrated on a periodically driven quantum dot in contact with two electron reservoirs and optimization protocols are discussed.

I. INTRODUCTION

Due to the seminal work of primarily Onsager and Prigogine, the theory of linear irreversible thermodynamics has become one of the cornerstones of modern statistical physics. Close to equilibrium, one can use this framework to determine the thermodynamic fluxes, such as heat and work, and show that they satisfy general properties, such as Onsager symmetry and the Green-Kubo relations [1].

Over the last two decades, a somewhat different approach has been undertaken to study the thermodynamics of small-scaled systems [2,3]. This theory, known as stochastic thermodynamics, uses Markov dynamics to model systems at the mesoscale, where fluctuations in the thermodynamic fluxes become important. The assumption of local detailed balance then leads to a consistent definition of the thermodynamic properties of the system. The stochastic fluxes of the system satisfy general relations such as the Jarzynski equality [4,5]. Furthermore, this theory has lead to applications in several other branches of science, such as information theory [6], chemical reaction networks [7], and active matter [8,9].

A natural question to ask is how the classical ideas of linear irreversible thermodynamics can be incorporated in the theory of stochastic thermodynamics. This problem has been addressed for several case studies [10–21]. Furthermore, general theories have been derived for periodically driven systems in contact with a single reservoir [22–24], and for steady-state systems in contact with two reservoirs [25,26], leading to bounds the power and efficiency of thermodynamic engines [27–29]. A more general approach for systems with any number of reservoirs and time-dependent driving has not been studied thoroughly.

In this paper, we close this gap by deriving a general formalism for the linear thermodynamics of stochastic systems with both steady-state and time-periodic drivings. Our study is carried out by taking into account multiple heat and particle reservoirs. We obtain expressions for thermodynamic quantities, such as chemical work, heat, and entropy production in terms of equilibrium probability distribution and the drivings.

In particular, we show that general results of linear irreversible thermodynamics, such as the structure of entropy production rate and Onsager symmetry are valid for this general class of systems.

This paper is organized as follows. We start in Sec. II by introducing the model and by discussing its linearized dynamics. In Sec. III, we define the work and heat fluxes and show how they are related to the entropy production rate. The evaluation of Onsager coefficients and the existence of an Onsager-Casimir symmetry relation are discussed in Sec. IV. In Sec. V, we apply our formalism to a periodically driven two-level system. Conclusions and outlook are discussed in Sec. VI.

II. MODEL

Throughout this paper, we focus on systems with a discrete set of states in contact with multiple temperature and particle reservoirs that can induce transitions between distinct configurations. The system can be in a given state m, specified by its energy $\epsilon_m(t)$ and particle number n_m with probability $p_m(t)$. The time-evolution of $p_m(t)$ is described by a master equation

$$\dot{p}_m(t) = \sum_{n,j} W_{mn}^j(t) p_n(t), \qquad (1)$$

where $W_{mn}^j(t)$ is the probability per unit of time of a transition from a state n to a state m induced by reservoir j. Conservation of probability implies that

$$\sum_m W_{mn}^j(t) = 0, \qquad (2)$$

valid for all m, and therefore $W_{mm}^j(t) = -\sum_{n \neq m} W_{nm}^j(t)$.

Each reservoir j is characterized by a temperature $T_j(t)$ and chemical potential $\mu_j(t)$. If the system is in contact with a single reservoir with time-independent temperature T_j and chemical potential μ_j, it will converge to an equilibrium state

given by the Boltzmann-Gibbs distribution:

$$P_m^j = \frac{1}{Z_{eq}^j} e^{\frac{-(\epsilon_m - \mu_j n_m)}{T_j}}, \tag{3}$$

where $Z_{eq}^j = \sum_m e^{-(\epsilon_m - \mu_j n_m)/T_j}$ is the (grand-canonical) partition function. By definition, the above equilibrium distribution should satisfy the detailed balance condition, $W_{mn}^{j,eq} P_n^j - W_{nm}^{j,eq} P_m^j = 0$, implying the following ratio between the transition rates $W_{mn}^{j,eq}$ and $W_{nm}^{j,eq}$:

$$\frac{W_{mn}^{eq;j}}{W_{nm}^{eq;j}} = e^{-\{(\epsilon_m - \epsilon_n) - \mu_j(n_m - n_n)\}/T_j}. \tag{4}$$

This expression allows us to write the transition rate $W_{mn}^{eq;j}$ as follows:

$$W_{mn}^{eq;j} = C_{mn}^j \lambda_n^{eq;j}, \tag{5}$$

where $\lambda_n^{eq;j} = \exp\left((\epsilon_n - \mu_j n_n)/T_j\right)$ and C_{mn}^j is a matrix that quantifies the coupling strength between states m and n, in this way specifying the time-symmetric part of the dynamics [30]. Due to the assumption of local detailed balance and the properties of the transition matrix, C^j satisfies the following symmetry relations:

$$C_{mn}^j = C_{nm}^j, \quad C_{nn}^j = -\sum_{m \neq n} C_{mn}^j. \tag{6}$$

A. Linear description

As stated before, the system will reach an equilibrium Boltzmann state when it is in contact with a single reservoir at constant temperature and chemical potential. This is generally not the case when the system is in contact with multiple reservoirs or when the temperature and chemical potential are modulated time-periodically. In those cases, detailed balance is broken, and the system starts dissipating heat and producing entropy. As each reservoir operates independently, each transition rate $W_{mn}^j(t)$ has the same form as in Eq. (5), but with time-dependent parameters $\epsilon_m(t)$, $T_j(t)$, $\mu_j(t)$, and $C_{mn}^j(t)$. The total transition matrix is obtained by summing over all reservoirs, $W_{mn}(t) = \sum_j W_{mn}^j(t)$, where $W_{mn}^j(t)$ is given by Eq. (5) for every reservoir j.

The temperatures and chemical potentials are modulated time-periodically. We introduce the driving functions $g_{T_j}(t)$ and $g_{\mu_j}(t)$ as

$$\frac{1}{T_j(t)} = \frac{1}{T_{0,j}} + F_{T_j} g_{T_j}(t), \tag{7}$$

$$\mu_j(t) = \mu_{0,j} + T_{0,j} F_{\mu_j} g_{\mu_j}(t), \tag{8}$$

where F_{α_j}'s correspond to the strength of the thermodynamic drivings $\alpha_j \in \{T_j, \mu_j\}$. The energy of each microscopic state is also driven periodically by an external work source,

$$\epsilon_n(t) = \epsilon_{0,n} + T_{0,j} F_\epsilon \gamma_{\epsilon,n} g_\epsilon(t), \tag{9}$$

where $\gamma_{\epsilon,n}$ is the amplitude with which the level n is modulated. As we are focusing on the regime close to equilibrium, both temperature and chemical potential modulations are assumed to be around the same equilibrium state for all reservoirs, $T_{0,j} = T_0$ and $\mu_{0,j} = \mu_0$ for all j.

To make further progress, we assume that the thermodynamic forces are sufficiently small so that we can perform a linear approximation. This is the crucial assumption for the theory of linear irreversible thermodynamics [1]. By expanding the coupling matrix C up to first-order with respect to modulations of temperature, chemical potential and energy, we have that

$$C_{mn}^j(t) = C_{mn}^{eq,j} + \sum_{\alpha,j} F_{\alpha_j} g_{\alpha_j}(t) C_{mn}^{\alpha_j}. \tag{10}$$

The perturbed coupling matrices C^{α_j} should satisfy the same symmetry relations as the unperturbed coupling matrices, Eq. (6). They are used for obtaining the following linear expression for $W_{mn}^j(t)$ in terms of thermodynamic forces:

$$W_{mn}^j(t) = W_{mn}^{eq,j} + \sum_\alpha F_{\alpha_j} W_{mn}^{\alpha_j}(t), \tag{11}$$

where

$$W_{mn}^{\alpha;j}(t) = g_{\alpha_j}(t) \left[W_{mn}^{eq,j} \gamma_n^\alpha + C_{mn}^{\alpha_j} \lambda_n^{eq;j} \right], \tag{12}$$

and the vector γ^α has elements given by

$$\gamma_n^\alpha = \begin{cases} (\epsilon_{0,n} - \mu_0 n_n) & \alpha = T_j \\ \gamma_{\epsilon,n} & \alpha = \epsilon \\ -n_n & \alpha = \mu_j. \end{cases} \tag{13}$$

Since the driving functions $g_{\alpha_j}(t)$ are assumed to be time periodic, $g_{\alpha_j}(t + \mathcal{T}) = g_{\alpha_j}(t)$ with $\mathcal{T}$ being the period of the driving, the system will relax to a time-periodic steady-state distribution. This distribution can be expanded up to linear order in terms of the thermodynamic forces [24],

$$p(t) = p^{eq} + \sum_{\alpha,j} F_{\alpha_j} p^{\alpha_j}(t), \tag{14}$$

where p^{eq} is the Boltzmann-Gibbs distribution associated to the reference energy, temperature and chemical potential, $\epsilon_{0,n}$, T_0, and μ_0, respectively. Substituting Eq. (14) into the master equation (1) leads to

$$\dot{p}^{\alpha_j}(t) = W^{eq} p^{\alpha_j}(t) + W^{\alpha_j}(t) p^{eq}. \tag{15}$$

Thus, the first-order contribution in the probability $\dot{p}^{\alpha_j}(t)$ depends only on the total equilibrium matrix $W_{mn}^{eq} = \sum_j W_{mn}^{eq,j}$ and on the linear perturbation matrix $W^{\alpha_j}(t)$ evaluated over the equilibrium probability. The above expression can be integrated, leading to

$$p^{\alpha_j}(t) = \int_0^\infty d\tau \, e^{W^{eq}\tau} W^{\alpha_j}(t - \tau) p^{eq}, \tag{16}$$

which is time-periodic. Inserting the explicit formula for $W^{\alpha_j}(t)$ and once again taking into account the properties of the coupling matrix given by Eq. (6), we arrive at the final expression for the component $p^{\alpha_j}(t)$:

$$p^{\alpha_j}(t) = \int_0^\infty d\tau \, e^{W^{eq}\tau} W^{eq,j} \gamma^\alpha p^{eq} g_{\alpha_j}(t - \tau), \tag{17}$$

i.e., the first order correction in the coupling matrix does not contribute to $p^{\alpha_j}(t)$. This is a manifestation of the fact that the time-symmetric part of the dynamics does not contribute to the linear response [30]. We conclude that, up to first-order, the time-periodic steady-state distribution can be obtained

exactly in terms of the equilibrium properties, the driving function $g_\alpha(t)$'s and the γ_α's.

Finally, it is worth mentioning that Eq. (17) reduces to the one obtained in Ref. [24] for the one reservoir case.

III. THERMODYNAMIC FLUXES

Having developed a general formalism to derive the linear dynamics of the system under study, we are now ready to evaluate the thermodynamic properties, using the framework of stochastic thermodynamics [2,3]. In particular, the direct work rate $\dot{W}_d(t)$, chemical work flux $\dot{W}_{\text{chem}}(t)$, and the heat flux $\dot{Q}(t)$ are given by

$$\dot{W}_d(t) = \sum_m \dot{\epsilon}_m(t) p_m(t), \tag{18}$$

$$\dot{W}_{\text{chem}}(t) = \sum_{m,j} \mu_j(t) n_m \dot{p}_m^j(t), \tag{19}$$

$$\dot{Q}(t) = \sum_{m,j} [\epsilon_m - \mu_j(t) n_m] \dot{p}_m^j(t) \tag{20}$$

with

$$\dot{p}_m^j(t) = \sum_n W_{mn}^j(t) p_n(t). \tag{21}$$

The time evolution of the mean internal energy of the system $U(t) = \sum_m \epsilon_m(t) p_m(t)$ is given by

$$\dot{U}(t) = \dot{W}_d(t) + \dot{W}_{\text{chem}}(t) + \dot{Q}(t), \tag{22}$$

in agreement with the first law of thermodynamics. By inserting Eq. (9) into Eq. (18), the average direct work per unit of time can be written as

$$\dot{\bar{W}}_d = \frac{T_0 F_\epsilon}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, \dot{g}_\epsilon(t) \sum_m \gamma_{\epsilon,m} p_m(t). \tag{23}$$

Equation (23) is conveniently rewritten as a product of forces and flux, $\dot{\bar{W}}_d = T_0 F_\epsilon J_\epsilon$, with work flux J_ϵ given by

$$J_\epsilon = -\frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, g_\epsilon(t) \sum_m \gamma_{\epsilon,m} \dot{p}_m(t), \tag{24}$$

where a partial integration was performed taking into account the periodicity of $p_m(t)$. One can decompose it further as

$$J_\epsilon = \sum_j J_{\epsilon_j} \tag{25}$$

with J_{ϵ_j} given by

$$J_{\epsilon_j} = -\frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, g_\epsilon(t) \sum_{m,n} \gamma_{\epsilon_j,m} W_{mn}^j(t) p_n(t), \tag{26}$$

and $T_0 F_\epsilon J_{\epsilon_j}$ can be interpreted as the direct work delivered to reservoir j.

Proceeding analogously, the total mean chemical work per cycle can be obtained by integrating Eq. (19) over one period and subtracting $\mu_0 \sum_j \int_0^{\mathcal{T}} \dot{p}_m^j(t) dt = 0$, which gives

$$\dot{\bar{W}}_{\text{chem}} = T_0 \sum_j F_{\mu_j} J_{\mu_j}, \tag{27}$$

where J_{μ_j} is defined as

$$J_{\mu_j} = -\frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, g_{\mu_j}(t) \sum_{m,n} \gamma_{\mu_j,m} W_{mn}^j(t) p_n(t). \tag{28}$$

Since the driving is periodic, the average internal energy of the system does not change over a period of the driving, $\dot{\bar{U}} = 0$. The first law of thermodynamics then leads to an expression for the average heat in terms of fluxes,

$$\dot{\bar{Q}} = -\dot{\bar{W}}_d - \dot{\bar{W}}_{\text{chem}} = -T_0 \sum_j \left(F_{\epsilon_j} J_{\epsilon_j} + F_{\mu_j} J_{\mu_j}\right). \tag{29}$$

This expression can also be evaluated by a direct integration of Eq. (20) over one period and summing over the contribution of all reservoirs.

The total entropy production $\bar{\sigma}$ is given by the sum of the contribution of all reservoirs

$$\bar{\sigma} = \sum_j \bar{\sigma}^j, \tag{30}$$

where each term $\bar{\sigma}^j$ can be calculated through the microscopic formula [31,32]

$$\bar{\sigma}^j = \frac{1}{\mathcal{T}} \sum_{m,n} \int_0^{\mathcal{T}} dt\, W_{mn}^j p_n \ln \frac{W_{mn}^j p_n}{W_{nm}^j p_m}. \tag{31}$$

Due to periodicity of the steady-state, the integral $\int_0^{\mathcal{T}} dt \sum_{m,n} W_{mn}^j p_n \ln(p_n/p_m)$ is strictly zero and Eq. (31) then reduces to

$$\bar{\sigma}^j = \frac{1}{\mathcal{T}} \sum_{m,n} \int_0^{\mathcal{T}} dt\, W_{mn}^j p_n \ln \frac{W_{mn}^j}{W_{nm}^j}. \tag{32}$$

Since the ratio between W_{mn}^j and W_{nm}^j is given by the local detailed balance condition, we can derive an expression for $\bar{\sigma}^j$ in terms of thermodynamic variables,

$$\begin{aligned} \bar{\sigma}^j &= -\frac{1}{\mathcal{T}} \sum_m \int_0^{\mathcal{T}} dt \left[\frac{\epsilon_m(t) - \mu_j(t) n_m}{T_j(t)}\right] \dot{p}_m^j \\ &= -\frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, \frac{\dot{Q}_j(t)}{T_j(t)}, \end{aligned} \tag{33}$$

in agreement with the classical thermodynamic definition of entropy production [33].

By inserting the expressions for heat and temperature from Eqs. (7) and (20), we have that

$$\bar{\sigma} = -\sum_j \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt \sum_m [\epsilon_m(t) - \mu_j(t) n_m] \dot{p}_m^j(t)$$

$$\times \left[\frac{1}{T_0} + F_{T_j} g_{T_j}(t)\right]. \tag{34}$$

This suggests the introduction of a new thermodynamic flux,

$$J_{T_j} = -\frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, g_{T_j}(t) \sum_{m,n} \gamma_{T_j,m} W_{mn}^j(t) p_n(t), \tag{35}$$

which allows us to rewrite the stochastic thermodynamics formula for entropy production to a bilinear function of

thermodynamic forces and fluxes given by

$$\bar{\sigma} = \sum_j (F_{\epsilon_j} J_{\epsilon_j} + F_{\mu_j} J_{\mu_j} + F_{T_j} J_{T_j}) \qquad (36)$$

with $F_{\epsilon_j} = F_\epsilon$. This is in agreement with classical non-equilibrium thermodynamics [1].

It is worth noting that the structure of Eq. (35) clearly mimics that of the work and chemical fluxes, Eqs. (28) and (26). In fact one can easily verify that all three types of thermodynamic fluxes are of the form

$$J_{\alpha_j} = -\frac{1}{\mathscr{T}} \int_0^{\mathscr{T}} dt \, g_{\alpha_j}(t) \sum_{m,n} \gamma_m^\alpha W_{mn}^j(t) p_n(t) \qquad (37)$$

with $\alpha = T, \epsilon, \mu$.

IV. ONSAGER COEFFICIENTS

As the thermodynamic fluxes vanish in the absence of thermodynamic forces, one expects that they depend linearly on the thermodynamic forces F_β near equilibrium, which implies the following form for a flux J_α:

$$J_\alpha = \sum_\beta L_{\alpha,\beta} F_\beta, \qquad (38)$$

where $L_{\alpha,\beta}$ are the so-called Onsager coefficients. From Eq. (36), the entropy production rate $\bar{\sigma}$ is depicted as a quadratic function of the thermodynamic forces,

$$\bar{\sigma} = \sum_{\alpha,\beta} F_\alpha L_{\alpha,\beta} F_\beta. \qquad (39)$$

In the absence of odd parity variables (such as magnetic fields), the Onsager coefficients of steady-state systems generally satisfy the Onsager reciprocal relations, $L_{\alpha,\beta} = L_{\beta,\alpha}$. This is no longer the case for systems with time-dependent driving, since the driving breaks the time-reversal symmetry. In this instance, Onsager symmetry is replaced by the weaker Onsager-Casimir symmetry, which relates the Onsager coefficients under time-forward driving to the cross-coefficient of time-inverted driving,

$$L_{\alpha,\beta} = \tilde{L}_{\beta,\alpha}, \qquad (40)$$

where the tilde stands for time inverted driving, $\tilde{g}_\alpha(t) = g_\alpha(-t)$.

Our aim here is to evaluate the Onsager coefficients and to prove the Onsager-Casimir reciprocal relations for a periodically driven system in contact with multiple reservoirs. By expanding Eq. (37) up to first order in the thermodynamic forces, we verify that J_α has two terms, one associated with the first order expansion of the transition matrix W_{mn}^j [from Eqs. (11) and (12)] and the other with the expansion of the probability distribution $p_n(t)$ [from Eq. (17)]. The total flux then reads $J_{\alpha_j} = J_{\alpha_j}^{(1)} + J_{\alpha_j}^{(2)}$ with

$$J_{\alpha_j}^{(1)} = -\sum_\beta \left[\frac{1}{\mathscr{T}} \int_0^{\mathscr{T}} dt \, g_{\alpha_j}(t) g_{\beta_j}(t) \sum_{m,n} \gamma_m^\alpha W_{mn}^{eq,j} \gamma_n^\beta p_n^{eq} \right] F_{\beta_j}, \qquad (41)$$

and

$$J_{\alpha_j}^{(2)} = -\sum_{\beta,j'} \left[\frac{1}{\mathscr{T}} \int_0^{\mathscr{T}} dt \int_0^\infty d\tau \, g_{\alpha_j}(t) g_{\beta_{j'}}(t-\tau) \right.$$
$$\left. \times \sum_{k,l,m,n} \gamma_m^\alpha W_{mn}^{eq,j} (e^{W^{eq}\tau})_{nk} W_{kl}^{eq,j'} \gamma_l^\beta p_l^{eq} \right] F_{\beta_{j'}}, \qquad (42)$$

respectively. One can easily see that the first flux depends solely on the thermodynamic forces associated with the same reservoir, while the second flux is dependent on all thermodynamic forces. Using the linearized expressions, one can now associate an Onsager matrix with each of those fluxes, $J_{\alpha_j}^{(1)} = \sum_\beta L_{\alpha_j,\beta_j}^{(1)} F_{\beta_j}$ and $J_{\alpha_j}^{(2)} = \sum_{\beta,j'} L_{\alpha_j,\beta_{j'}}^{(2)} F_{\beta_{j'}}$, where the Onsager coefficients are given by

$$L_{\alpha_j,\beta_j}^{(1)} = -\frac{1}{\mathscr{T}} \int_0^{\mathscr{T}} dt \, g_{\alpha_j}(t) g_{\beta_j}(t) \sum_{m,n} \gamma_m^\alpha W_{mn}^{eq,j} \gamma_n^\beta p_n^{eq} \qquad (43)$$

and

$$L_{\alpha_j,\beta_{j'}}^{(2)} = -\frac{1}{\mathscr{T}} \int_0^{\mathscr{T}} dt \int_0^\infty d\tau \, g_{\alpha_j}(t) g_{\beta_{j'}}(t-\tau)$$
$$\times \sum_{k,l,m,n} \gamma_m^\alpha W_{mn}^{eq,j} (e^{W^{eq}\tau})_{nk} W_{kl}^{eq,j'} \gamma_l^\beta p_l^{eq} \qquad (44)$$

with $L_{\alpha_j,\beta_{j'}}^{(1)} = 0$ for $j \neq j'$. The total Onsager matrix is the sum of these two matrices, $L_{\alpha_j,\beta_{j'}} = L_{\alpha_j,\beta_{j'}}^{(1)} + L_{\alpha_j,\beta_{j'}}^{(2)}$. This structure for the Onsager coefficients resembles the one found for a class of quantum mechanical systems studied in [16].

We are now ready to study the reciprocal relations for $L_{\alpha_j,\beta_j}^{(1)}$ and $L_{\alpha_j,\beta_{j'}}^{(2)}$. Remarkably, both Onsager matrices will satisfy an Onsager-Casimir relation separately, which implies that the total Onsager matrix will satisfy the same Onsager-Casimir symmetry. We first look at $L_{\alpha_j,\beta_j}^{(1)}$. One can easily verify that these coefficients are invariant under time-reversal by replacing $g_\alpha(t)$ and $g_\beta(t)$ by $g_\alpha(-t)$ and $g_\beta(-t)$ and doing a change of integration variable to $t' = -t$. Subsequently, taking into account the detailed balance condition, one can show that $\sum_{m,n} \gamma_n^\beta W_{nm}^{eq,j} \gamma_m^\alpha p_m^{eq} = \sum_{m,n} \gamma_m^\alpha W_{mn}^{eq,j} \gamma_n^\beta p_n^{eq}$ and hence the right-hand side of Eq. (43) becomes

$$L_{\alpha_j,\beta_j}^{(1)} = -\frac{1}{\mathscr{T}} \int_0^{\mathscr{T}} dt \, \tilde{g}_{\beta_j}(t) \tilde{g}_{\alpha_j}(t) \sum_{m,n} \gamma_n^\beta W_{nm}^{eq,j} \gamma_m^\alpha p_m^{eq}$$
$$= \tilde{L}_{\beta_j,\alpha_j}^{(1)}, \qquad (45)$$

which proves the Onsager-Casimir symmetry for $L_{\alpha_j,\beta_j}^{(1)}$.

The proof of the second term can be done in a similar way. We start by taking the time transformation $-t = t' - \tau$ in Eq. (44),

$$L_{\alpha_j,\beta_{j'}}^{(2)} = \left[\frac{1}{\mathscr{T}} \int_0^\infty d\tau \int_\tau^{-\mathscr{T}+\tau} dt' \, g_{\alpha_j}(-t'+\tau) g_{\beta_{j'}}(-t') \right.$$
$$\left. \times \sum_{k,l,m,n} \gamma_m^\alpha W_{mn}^{eq,j} (e^{W^{eq}\tau})_{nk} W_{kl}^{eq,j'} \gamma_l^\beta p_l^{eq} \right]. \qquad (46)$$

Due to the periodicity of the drivings, the first integral can be shifted by $\mathscr{T} - \tau$, allowing us to rewrite it as

$$L^{(2)}_{\alpha_j,\beta_{j'}} = -\left[\frac{1}{\mathscr{T}}\int_0^{\mathscr{T}} dt' \int_0^\infty d\tau\, \tilde{g}_{\alpha_j}(t'-\tau)\tilde{g}_{\beta_{j'}}(t')\right.$$
$$\left. \times \sum_{k,l,m,n} \gamma_m^\alpha W^{eq,j}_{mn}(e^{W^{eq}\tau})_{nk} W^{eq,j'}_{kl}\gamma_l^\beta p_l^{eq}\right]. \quad (47)$$

By once again appealing to the detailed balance condition, one can show that

$$\sum_{k,l,m,n} \gamma_m^\alpha W^{eq,j}_{mn}(e^{W^{eq}\tau})_{nk} W^{eq,j'}_{kl}\gamma_l^\beta p_l^{eq}$$
$$= \sum_{k,l,m,n} \gamma_l^\beta W^{eq,j'}_{lk}(e^{W^{eq}\tau})_{kn} W^{eq,j}_{nm}\gamma_m^\alpha p_m^{eq}, \quad (48)$$

and hence $L^{(2)}_{\alpha_j,\beta_{j'}}$ becomes

$$L^{(2)}_{\alpha_j,\beta_{j'}} = -\left[\frac{1}{\mathscr{T}}\int_0^{\mathscr{T}} dt' \int_0^\infty d\tau\, \tilde{g}_{\beta_{j'}}(t')\tilde{g}_{\alpha_j}(t'-\tau)\right.$$
$$\left. \times \sum_{k,l,m,n} \gamma_l^\beta W^{eq,j'}_{lk}(e^{W^{eq}\tau})_{kn} W^{eq,j}_{nm}\gamma_m^\alpha p_m^{eq}\right]. \quad (49)$$

The right-hand side of Eq. (49) is just the Onsager coefficient $\tilde{L}^{(2)}_{\beta_{j'},\alpha_j}$. This completes the proof of the Onsager-Casimir symmetry. We note that this symmetry relation can alternatively be proven using the fluctuation theorem [34].

These results also implies an Onsager-Casimir relation for any combination of $J_{\alpha,i}$'s. For example, we define

$$J_i' = \sum_{\alpha,j} A_{i;\alpha,j} J_{\alpha,j}, \quad (50)$$

for some matrix A, where we assume A to be invertible. The associated thermodynamic forces are given by

$$F_i' = \sum_{\alpha,j} (A^{-1})_{\alpha,j;i} J_{\alpha,j}, \quad (51)$$

as the entropy production rate $\sigma = \sum_i F_i' J_i'$ is independent of the choice of J's. The new Onsager matrix L' is of the form

$$L' = ALA^\dagger, \quad (52)$$

and one can straightforwardly verify that this matrix should satisfy the same Onsager-Casimir relations as the original matrix L. This statement can be extended for matrices A that are not invertible, as was shown in [7,35]. In particular, we can conclude that Onsager-Casimir symmetry is also valid when one only looks at the total fluxes J_ϵ, J_μ, and J_T.

V. TWO LEVEL SYSTEMS

As an example, we consider a quantum dot, with one active energy level, in contact with two electron reservoirs at temperatures $T_1(t)$ and $T_2(t)$ and chemical potentials $\mu_1(t)$ and $\mu_2(t)$, respectively. The quantum dot can be empty or occupied by a single electron with probabilities $p_0(t)$ and $p_1(t) = 1 - p_0(t)$, respectively. The temperature and chemical of the electron reservoirs as well as the energy of the quantum dot are modulated according to Eqs. (7)–(9), respectively. The total transition matrix $W(t)$ is the sum of both reservoir contributions $W(t) = W^1(t) + W^{(2)}(t)$ with $W^j(t)$ given by

$$W^j(t) = \begin{pmatrix} -\Gamma_j y(t) & \Gamma_j(1-y(t)) \\ \Gamma_j y(t) & -\Gamma_j(1-y(t)) \end{pmatrix},$$

where Γ_j describes the interaction between the quantum dot and the j-th reservoir and $y(t)$ is the Fermi-Dirac distribution $y(t) = [1 + \exp((\epsilon(t) - \mu(t))/T(t))]^{-1}$.

For simplicity, we set $F_{\mu_j} = 0$, implying that the chemical potentials of both reservoirs are the same and thereby $\dot{W}_{chem} = 0$. The thermodynamic variables are modulated via the driving functions $g_\epsilon(t) = \sqrt{2}\sin(\omega t + \phi)$ and $g_{T_j}(t) = \sqrt{2}\sin(\omega t)$, respectively, where we have assumed that both reservoirs and the electron level are all driven with the same frequency $\omega = 2\pi/\mathscr{T}$, but with a phase-difference ϕ between the driving of the energy and the and temperature drivings.

The lowest order expressions for the energy and temperature fluxes J_ϵ and J_{T_j} and for the entropy production rate $\bar{\sigma}$ can now be calculated using the expressions from the previous section and are given by

$$J_\epsilon = \frac{2\pi p_0^{eq} p_1^{eq}}{\mathscr{T}(4\pi^2 + \tilde{\chi}^2)}[2\pi F_\epsilon \tilde{\chi} + (\epsilon_0 - \mu_0)(\tilde{\chi}\sin\phi + 2\pi\cos\phi)](F_{T_1}\chi_1 + F_{T_2}\chi_2)], \quad (53)$$

$$J_{T_1} = \frac{p_0^{eq} p_1^{eq}(\epsilon_0 - \mu_0)\chi_1}{\mathscr{T}(4\pi^2 + \tilde{\chi}^2)}[F_\epsilon(4\pi^2\cos\phi - 2\pi\tilde{\chi}\sin\phi) + (\epsilon_0 - \mu_0)\tilde{\chi}\chi_2(F_{T_1} - F_{T_2}) + 4\pi^2(\epsilon_0 - \mu_0)F_{T_1}], \quad (54)$$

$$\bar{\sigma} = \frac{4\pi^2 p_0^{eq} p_1^{eq}}{\mathscr{T}(4\pi^2 + \tilde{\chi}^2)}\left[F_\epsilon^2\tilde{\chi} + (\epsilon_0 - \mu_0)^2(F_{T_1}^2\chi_1 + F_{T_2}^2\chi_2) + 2(\epsilon_0 - \mu_0)\cos\phi F_\epsilon(F_{T_1}\chi_1 + F_{T_2}\chi_2) + \frac{(\epsilon_0 - \mu_0)^2}{4\pi^2}\chi_1\chi_2\tilde{\chi}(F_{T_1} - F_{T_2})^2\right], \quad (55)$$

respectively, where $\chi_j = \Gamma_j\mathscr{T}$ and $\tilde{\chi} = (\Gamma_1 + \Gamma_2)\mathscr{T}$. For the special case, $F_{T_1} = F_{T_2}$ and $\Gamma_1 = \Gamma_2$, the above expressions reduce to the single reservoir case up to a factor 2 [24]. J_{T_2} has a similar expression as J_{T_1} with T_1 and T_2, F_1 and F_2 interchanged. One can

easily verify that these expressions satisfy Onsager-Casimir symmetry.

These results can be used to optimize the amount of direct work, $\dot{W}_d = T_0 F_\epsilon J_\epsilon$ that can be done by the system. In particular, an optimization with respect to F_ϵ yields the following
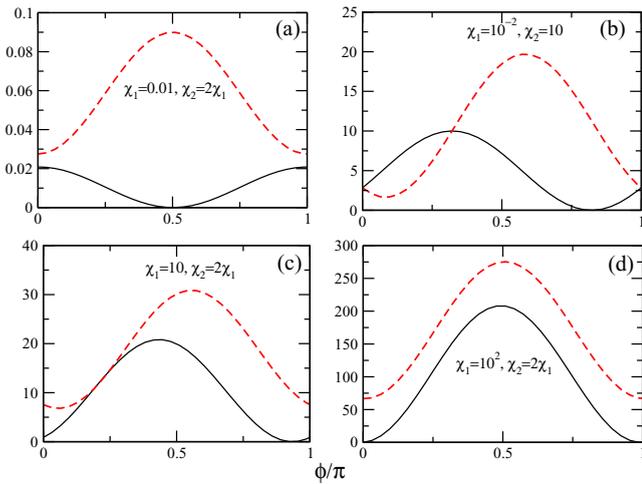
FIG. 1. Reduced dissipated power $-\dot{W}\mathscr{T}/(T_0 p_0^{eq} p_1^{eq} F_{T_1}^2)$ (continuous lines) and entropy production $\bar{\sigma}\mathscr{T}/(p_0^{eq} p_1^{eq} F_{T_1}^2)$ (dashed lines) versus ϕ for distinct values of couplings χ_1 and χ_2. In all cases we considered $F_{T_2} = 2F_{T_1}$.

relation for the maximum direct power:

$$-\dot{W}_{d;\max} = \frac{p_0^{eq} p_1^{eq} T_0 (\epsilon_0 - \mu_0)^2 (F_{T_1}\chi_1 + F_{T_2}\chi_2)^2}{4\tilde{\chi}\mathscr{T}(4\pi^2 + \tilde{\chi}^2)}$$
$$\times (\tilde{\chi}\sin\phi + 2\pi\cos\phi)^2. \qquad (56)$$

Figure 1 depicts the behavior of σ and $\dot{W}$ versus ϕ for distinct couplings χ_1 and χ_2 with F_ϵ given by its optimal value. In the limit of low (large) "effective" couplings, $\tilde{\chi} \ll 1$ ($\tilde{\chi} \gg 1$), the work output is maximal (minimum) when the driving of the work source is in phase with that of the heat sources, $\phi = 0$ and minimum (maximum) when the driving is out of phase, $\phi = \pi/2$, in accordance with Eq. (56). Conversely, for the above choice of F_ϵ, the positions of maxima and minima of the entropy production fulfill the above relation

$$\tan\phi = \left\{ -\frac{\tilde{\chi}^2 + 12\pi^2 \pm \sqrt{\tilde{\chi}^4 + 40\tilde{\chi}^2\pi^2 + 144\pi^4}}{4\pi\tilde{\chi}} \right\}, \quad (57)$$

where $+(-)$ denote to the maximum (minimum). They approach $\pi/2$ (maximum) and $\phi = 0$ (minimum) for $\tilde{\chi} \ll 1$

and $\tilde{\chi} \gg 1$, respectively and deviate from these limits for intermediate coupling sets.

Similar analytic optimizations for other thermodynamic fluxes can also be performed. For instance, by optimizing $\dot{W}$ with respect to both F_ϵ and the phase-difference ϕ, the expression for $\dot{W}_{\max}$ becomes

$$-\dot{W}_{d;\max} = \frac{p_0^{eq} p_1^{eq} T_0 (\epsilon_0 - \mu_0)^2 (F_{T_1}\chi_1 + F_{T_2}\chi_2)^2}{4\tilde{\chi}\mathscr{T}}, \quad (58)$$

where the optimal phase-difference and amplitude are given by

$$\tan\phi = \left(\frac{\tilde{\chi}}{2\pi}\right), \qquad (59)$$

$$F_\epsilon = -\frac{(\epsilon_0 - \mu_0)}{4\pi\tilde{\chi}}\sqrt{4\pi^2 + \tilde{\chi}^2}(F_{T_1}\chi_1 + F_{T_2}\chi_2). \quad (60)$$

VI. CONCLUSIONS

In this paper, we have derived a general linear description for the thermodynamics of Markov systems in contact to multiple reservoirs, using the framework of stochastic thermodynamics. We have shown that the thermodynamic fluxes such as direct and chemical work and heat, can be written in a general form, as functions of the driving and the equilibrium properties of the system. The entropy production is obtained as a bilinear function of thermodynamic forces and associated fluxes. Furthermore, we calculated all Onsager coefficients and showed that they satisfy a generalized Onsager-Casimir relation.

Finally, we mention some interesting directions for further research. Firstly, it would be interesting to extend our analysis to higher order response coefficients and to study the resulting constraints on heat engines [36,37]. Secondly, it would be very interesting to see if our results can be extended to quantum mechanical systems and systems with strong coupling [38,39]. Finally, it should be no problem to test our predictions, such as the generalized Onsager-Casimir relation, with state-of-the-art experimental setups [40,41].

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