CORE

# Thermodynamics of Micro- and Nano-Systems Driven by Periodic Temperature Variations 

Kay Brandner, ${ }^{1}$ Keiji Saito, ${ }^{2}$ and Udo Seifert ${ }^{1}$<br>${ }^{1}$ II. Institut für Theoretische Physik, Universität Stuttgart, 70550 Stuttgart, Germany<br>${ }^{2}$ Department of Physics, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Japan 223-8522

(Received 21 May 2015; published 19 August 2015)


#### Abstract

We introduce a general framework for analyzing the thermodynamics of small systems that are driven by both a periodic temperature variation and some external parameter modulating their energy. This setup covers, in particular, periodic micro- and nano-heat engines. In a first step, we show how to express total entropy production by properly identified time-independent affinities and currents without making a linear response assumption. In linear response, kinetic coefficients akin to Onsager coefficients can be identified. Specializing to a Fokker-Planck-type dynamics, we show that these coefficients can be expressed as a sum of an adiabatic contribution and one reminiscent of a Green-Kubo expression that contains deviations from adiabaticity. Furthermore, we show that the generalized kinetic coefficients fulfill an Onsager-Casimir-type symmetry tracing back to microscopic reversibility. This symmetry allows for nonidentical off-diagonal coefficients if the driving protocols are not symmetric under time reversal. We then derive a novel constraint on the kinetic coefficients that is sharper than the second law and provides an efficiency-dependent bound on power. As one consequence, we can prove that the power vanishes at least linearly when approaching Carnot efficiency. We illustrate our general framework by explicitly working out the paradigmatic case of a Brownian heat engine realized by a colloidal particle in a time-dependent harmonic trap subject to a periodic temperature profile. This case study reveals inter alia that our new general bound on power is asymptotically tight.


DOI: 10.1103/PhysRevX.5.031019

## I. INTRODUCTION

Thermodynamic processes on the micro- and nano-scale in systems driven out of equilibrium by periodically changing control parameters such as an external force or the temperature of their environment can be scrutinized under the microscope by virtue of precise measurements of characteristic quantities such as applied work or exchanged heat [1-6]. Despite such ground-breaking results, so far, no general theoretical framework for the thermodynamic description of periodically driven systems beyond the quasistatic limit is available.

In principle, the concepts of irreversible thermodynamics, a phenomenological but powerful theory, which, building on the principle of local equilibrium, furnishes nonequilibrium steady states with a universal thermodynamics structure [7], can be transferred to periodic systems [8-10]. These results are, however, crucially tied to specific models and require rather involved and nonintuitive definitions for currents and affinities.

In this paper, we overcome these limitations. Starting from the first law formulated for an arbitrary system driven out of equilibrium by both periodic perturbations of its

[^0]Hamiltonian and the temperature of a surrounding heat bath, we obtain natural and perfectly general identifications of fluxes and affinities. Since they are defined on the level of cycle averages, these quantities are time independent. Nevertheless, our new formalism captures essential finitetime properties of the driven system and permits a discussion of quantities like power, which are out of reach for the laws of classical thermodynamics due to its notorious lack of time scales.

Moreover, our approach provides a universal prescription for the construction of kinetic coefficients, which fully characterize the system in the linear response regime. By using a well-established and rather general stochastic approach based on a Fokker-Planck equation to describe the underlying time-dependent dynamics [11], we prove that these coefficients are interrelated by a remarkable symmetry, which, just like Onsager's celebrated reciprocity relations [12,13], can be traced back to microscopic reversibility.

Ever since James Watt's steam engine, the urge to explore the fundamental principles governing the performance of cyclic heat engines was one of the major quests in thermodynamics. Two key figures of merit are particularly important in this context. While efficiency, the first one, is universally bounded by the Carnot value as a direct consequence of the second law, similar constraints on power, the second one, could, so far, be obtained only within specific setups (see, for example, Refs. [14-18]).

Thermoelectric heat engines, which, in contrast to cyclic ones, work in a steady state $[19,20]$, are likewise subject to substantial research efforts concerning efficiency [21,22], power [23,24], and the relation between these quantities [25,26]. At least in the linear response regime, however, much more general results are currently available for these types of heat engines than for their periodic counterparts. Specifically, it can be shown that, in the linear regime, the power of such devices is bounded by a quadratic function of efficiency that vanishes at the Carnot value $\eta_{\mathrm{C}}$ and attains its maximum at the Curzon-Ahlborn value $\eta_{\mathrm{C}} / 2$ [27-30]. This result follows from a quite general analysis within the framework of linear irreversible thermodynamics. It must, however, be reconsidered in the presence of a magnetic field, which breaks the Onsager symmetry, an issue which is currently under active discussion [20,31-40].

Here, by applying our new formalism, we establish the aforementioned quadratic bound on power for cyclic heat engines in linear response. In particular, by using a novel method, which does not require any additional assumptions, we prove that this bound still holds if the matrix of kinetic coefficients is not symmetric, which is the generic case for periodically driven systems. We emphasize that, by now, an analogous result for thermoelectric heat engines is not available on such a general level. To complete our analysis, we show that this bound on power is tight within a paradigmatic model of a Brownian heat engine, which was originally proposed in [14] and recently realized in a landmark experiment [2].

The rest of this paper is structured in three major parts. In Sec. II, we develop our general formalism and prove a generalized reciprocity relation for the kinetic coefficients of periodic systems. Section III is devoted to the discussion of cyclic heat engines in the linear response regime and the derivation of a general bound on power. We illustrate our results by considering a simple model system in Sec. IV. Finally, we conclude in Sec. V.

## II. FRAMEWORK

In this section, we demonstrate that the notions of irreversible thermodynamics can be transferred to periodically driven systems.

## A. Nonlinear regime

We begin with a brief review of the energetics of driven systems in thermal contact with a heat bath [30]. Specifically, we consider a classical system with degrees of freedom $\mathbf{x} \equiv\left(x_{1}, \ldots, x_{n}\right)$ and the time-dependent Hamiltonian

$$
\begin{equation*}
H(\mathbf{x}, t) \equiv H_{0}(\mathbf{x})+\Delta H g_{w}(\mathbf{x}, t) \tag{1}
\end{equation*}
$$

which is immersed in a heat bath, whose temperature $T(t)$ oscillates between the two values $T_{\mathrm{c}}$ and $T_{\mathrm{h}}>T_{\mathrm{c}}$. Here,
$g_{w}(\mathbf{x}, t)$ denotes an externally controlled dimensionless function of order 1 and $\Delta H$ quantifies the strength of this time-dependent perturbation. The power extracted by the controller thus reads

$$
\begin{equation*}
\dot{W}(t) \equiv-\int d^{n} \mathbf{x} \dot{H}(\mathbf{x}, t) p(\mathbf{x}, t) \tag{2}
\end{equation*}
$$

where $p(\mathbf{x}, t)$ denotes the normalized probability density to find the system in the state $\mathbf{x}$ at the time $t$ and dots indicate time derivatives throughout the paper. To compensate for this loss in internal energy,

$$
\begin{equation*}
U(t)=\int d^{n} \mathbf{x} H(\mathbf{x}, t) p(\mathbf{x}, t) \tag{3}
\end{equation*}
$$

the system picks up the heat

$$
\begin{equation*}
\dot{Q}(t) \equiv \int d^{n} \mathbf{x} H(\mathbf{x}, t) \dot{p}(\mathbf{x}, t) \tag{4}
\end{equation*}
$$

from the environment as stipulated by the first law

$$
\begin{equation*}
\dot{U}(t) \equiv \dot{Q}(t)-\dot{W}(t) \tag{5}
\end{equation*}
$$

We will now pass from time-dependent to constant variables by exploiting the periodic boundary conditions

$$
\begin{equation*}
H(\mathbf{x}, t+\mathcal{T})=H(\mathbf{x}, t) \quad \text { and } \quad T(t+\mathcal{T})=T(t) \tag{6}
\end{equation*}
$$

where $\mathcal{T}$ is the length of one operation cycle. Quite naturally, we invoke the assumption that, given these conditions, the time evolution of the probability density $p(\mathbf{x}, t)$ eventually converges to a periodic limit

$$
\begin{equation*}
p^{\mathrm{c}}(\mathbf{x}, t)=p^{\mathrm{c}}(\mathbf{x}, t+\mathcal{T}) \tag{7}
\end{equation*}
$$

as illustrated in Fig. 1 for a simple system. Once this periodic state is reached, the average entropy production per cycle arises solely because of heat exchange between the system and the environment since, because of the periodicity of the distribution $p^{c}(\mathbf{x}, t)$, no net entropy is generated in the system in a full cycle; i.e., we have

$$
\begin{equation*}
\dot{S}=-\frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \frac{\dot{Q}(t)}{T(t)} \tag{8}
\end{equation*}
$$

By inserting Eq. (4) into Eq. (8) and parametrizing $T(t)$ by a dimensionless function $0 \leq \gamma_{q}(t) \leq 1$ such that

$$
\begin{equation*}
T(t) \equiv \frac{T_{\mathrm{c}} T_{\mathrm{h}}}{T_{\mathrm{h}}+\left(T_{\mathrm{c}}-T_{\mathrm{h}}\right) \gamma_{q}(t)}, \tag{9}
\end{equation*}
$$

it is straightforward to derive the expression


FIG. 1. Nonequilibrium periodic state of a system with 1 degree of freedom $x$ in a sinusoidally shifted harmonic potential, represented by gray parabolas, which is embedded in an environment with periodically changing temperature as indicated by the periodic color gradient. The solid line in the $x$ - $t$ plane shows the motion of the center of the Gaussian phase-space distribution, which lags behind the position of the potential minimum shown as a dashed line. At any time $t$, the width of the colored region equals the width of the phase-space distribution, which varies according to the temperature.

$$
\begin{align*}
\dot{S}= & \frac{\Delta H}{T_{\mathrm{c}}} \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} \dot{g}_{w}(\mathbf{x}, t) p^{\mathrm{c}}(\mathbf{x}, t) \\
& +\left(\frac{1}{T_{\mathrm{c}}}-\frac{1}{T_{\mathrm{h}}}\right) \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} \gamma_{q}(t) H(\mathbf{x}, t) \dot{p}^{\mathrm{c}}(\mathbf{x}, t) \tag{10}
\end{align*}
$$

using one integration by parts with respect to time. The corresponding boundary terms vanish because of the periodicity of the involved quantities. Obviously, Eq. (10) can be cast in the generic form [7]

$$
\begin{equation*}
\dot{S}=\mathcal{F}_{w} J_{w}+\mathcal{F}_{q} J_{q} \tag{11}
\end{equation*}
$$

by identifying the work flux

$$
\begin{equation*}
J_{w} \equiv \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} \dot{g}_{w}(\mathbf{x}, t) p^{\mathrm{c}}(\mathbf{x}, t) \tag{12}
\end{equation*}
$$

the generalized heat flux

$$
\begin{equation*}
J_{q} \equiv \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} \gamma_{q}(t) H(\mathbf{x}, t) \dot{p}^{\mathrm{c}}(\mathbf{x}, t) \tag{13}
\end{equation*}
$$

and the affinities

$$
\begin{equation*}
\mathcal{F}_{w} \equiv \Delta H / T_{\mathrm{c}} \quad \text { and } \quad \mathcal{F}_{q} \equiv 1 / T_{\mathrm{c}}-1 / T_{\mathrm{h}} \tag{14}
\end{equation*}
$$

Within only a few lines, we have thus obtained our first main result; namely, we recovered for periodically time-dependent
systems, the structure of irreversible thermodynamics. The key point here is the identification of appropriate pairs of affinities and fluxes, whose respective products sum up to the total entropy production.

For later purposes, we note that, after one integration by parts with respect to $t$, the heat flux (13) can be rewritten as

$$
\begin{align*}
J_{q}= & \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} \dot{g}_{q}(\mathbf{x}, t) p^{\mathrm{c}}(\mathbf{x}, t) \\
& +\frac{\Delta H}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} \gamma_{q}(t) g_{w}(\mathbf{x}, t) \dot{p}^{\mathrm{c}}(\mathbf{x}, t) \tag{15}
\end{align*}
$$

where

$$
\begin{equation*}
g_{q}(\mathbf{x}, t) \equiv-H_{0}(\mathbf{x}) \gamma_{q}(t) \tag{16}
\end{equation*}
$$

## B. Linear response regime 1. Kinetic coefficients

We now focus on the linear regime with respect to the temporal gradients $\Delta H$ and $\Delta T \equiv T_{\mathrm{h}}-T_{\mathrm{c}}$. By expanding the fluxes (12) and (13), we obtain

$$
\begin{align*}
J_{w} & =L_{w w} \mathcal{F}_{w}+L_{w q} \mathcal{F}_{q}+\mathcal{O}\left(\Delta^{2}\right) \\
J_{q} & =L_{q w} \mathcal{F}_{w}+L_{q q} \mathcal{F}_{q}+\mathcal{O}\left(\Delta^{2}\right) \tag{17}
\end{align*}
$$

with linearized affinities

$$
\begin{equation*}
\mathcal{F}_{w}=\Delta H / T_{\mathrm{c}} \quad \text { and } \quad \mathcal{F}_{q}=\Delta T / T_{\mathrm{c}}^{2}+\mathcal{O}\left(\Delta^{2}\right) \tag{18}
\end{equation*}
$$

and kinetic coefficients

$$
\begin{equation*}
\left.L_{\alpha \beta} \equiv \frac{\partial J_{\alpha}}{\partial \mathcal{F}_{\beta}}\right|_{\mathcal{F}=0} \quad \text { for } \alpha, \beta=w, q \tag{19}
\end{equation*}
$$

The entropy production (8) thus reduces to

$$
\begin{equation*}
\dot{S}=\sum_{\alpha, \beta=w, g} L_{\alpha \beta} \mathcal{F}_{\alpha} \mathcal{F}_{\beta} \tag{20}
\end{equation*}
$$

To guarantee that this expression is non-negative for any $\mathcal{F}_{\alpha}$ as stipulated by the second law, the kinetic coefficients must obey the constraints

$$
\begin{equation*}
L_{w w}, L_{q q} \geq 0 \quad \text { and } \quad L_{w w} L_{q q}-\left(L_{w q}+L_{q w}\right)^{2} / 4 \geq 0 \tag{21}
\end{equation*}
$$

which we prove explicitly in Sec. III B for a large class of systems. It is, however, not evident at this stage whether a reciprocity relation relating $L_{\alpha \beta}$ with $L_{\beta \alpha}$ or any further constraints exists.

## 2. Adiabatic limit

As a first step, we investigate the adiabatic regime, which is characterized by the Hamiltonian $H(\mathbf{x}, t)$ and the temperature $T(t)$ changing slowly enough in time such that the system effectively passes through a sequence of equilibrium states, i.e.,

$$
\begin{equation*}
p^{\mathrm{c}}(\mathbf{x}, t)=\exp \left[-H(\mathbf{x}, t) /\left(k_{B} T(t)\right)\right] / Z(t) \tag{22}
\end{equation*}
$$

with

$$
\begin{equation*}
Z(t) \equiv \int d^{n} \mathbf{x} \exp \left[-H(\mathbf{x}, t) /\left(k_{B} T(t)\right)\right] \tag{23}
\end{equation*}
$$

and $k_{B}$ denoting Boltzmann's constant. Expanding Eq. (22) to linear order in $\Delta H$ and $\Delta T$ and inserting the result into Eqs. (12), (15) and (19) gives the universal expression

$$
\begin{equation*}
L_{\alpha \beta}^{\mathrm{ad}}=-\frac{1}{k_{B}}\left\langle\left\langle\delta \dot{g}_{\alpha} \delta g_{\beta}\right\rangle\right\rangle \tag{24}
\end{equation*}
$$

for the adiabatic kinetic coefficients. Here, we introduced the notations

$$
\begin{align*}
\langle\langle A\rangle\rangle & \equiv \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t\langle A(t)\rangle \\
& \equiv \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} A(\mathbf{x}, t) p^{\mathrm{eq}}(\mathbf{x}) \tag{25}
\end{align*}
$$

and

$$
\begin{equation*}
\delta A(\mathbf{x}, t) \equiv A(\mathbf{x}, t)-\langle A(\mathbf{x}, t)\rangle \tag{26}
\end{equation*}
$$

for any quantity $A(\mathbf{x}, t)$ and the equilibrium distribution of the unperturbed system

$$
\begin{equation*}
p^{\mathrm{eq}}(\mathbf{x}) \equiv \exp \left[-H_{0}(\mathbf{x}) /\left(k_{B} T_{\mathrm{c}}\right)\right] / Z_{0} \tag{27}
\end{equation*}
$$

with $Z_{0}$ denoting the canonical partition function.
Notably, the coefficients (24) are fully antisymmetric, i.e.,

$$
\begin{equation*}
L_{\alpha \beta}^{\mathrm{ad}}=-L_{\beta \alpha}^{\mathrm{ad}} \tag{28}
\end{equation*}
$$

As might be expected, this property, which can be proven by a simple integration by parts with respect to $t$, implies vanishing entropy production (20) in the adiabatic limit. This avoidance of dissipation can, however, only be achieved for an infinite cycle duration $\mathcal{T}$ and therefore inevitably comes with vanishing fluxes $J_{\alpha}$.

## 3. Stochastic dynamics

For further investigations of the kinetic coefficients, we have to specify the dynamics, which governs the time evolution of the probability density $p(\mathbf{x}, t)$. Having in
mind, in particular, mesoscopic systems surrounded by a fluctuating medium, a suitable choice is given by the Fokker-Planck equation [41]

$$
\begin{equation*}
\partial_{t} p(\mathbf{x}, t)=\mathrm{L}(\mathbf{x}, t) p(\mathbf{x}, t) \tag{29}
\end{equation*}
$$

with

$$
\begin{equation*}
\mathrm{L}(\mathbf{x}, t) \equiv-\partial_{x_{i}} D_{i}(\mathbf{x}, H, T)+\partial_{x_{i}} \partial_{x_{j}} D_{i j}(\mathbf{x}, H, T) \tag{30}
\end{equation*}
$$

where summation over identical indices is understood and natural boundary conditions are assumed. The Hamiltonian $H(\mathbf{x}, t)$ and the temperature $T(t)$ enter via the drift and diffusion coefficients $D_{i}(\mathbf{x}, H, T)$ and $D_{i j}(\mathbf{x}, H, T)$, which thus become implicitly time dependent [42].

We will now formulate a set of conditions on the general Fokker-Planck operator (30) to adapt it to the physical situation that we wish to discuss here. Since micro-reversibility plays a crucial role in linear irreversible thermodynamics, we have to ensure that our theory complies with this fundamental principle. To this end, first, at any time $t$, any possible state $\mathbf{x}$ of the system must be associated with the same energy as the time-reversed state $\boldsymbol{\varepsilon} \mathbf{x} \equiv\left(\varepsilon_{1} x_{1}, \ldots, \varepsilon_{n} x_{n}\right)$ with $\varepsilon_{i}=1$ for even and $\varepsilon_{i}=$ -1 for odd variables, i.e.,

$$
\begin{equation*}
H(\mathbf{x}, t)=H(\mathbf{\varepsilon} \mathbf{x}, t) \tag{31}
\end{equation*}
$$

where, throughout the paper, the transformation $\mathbf{x} \rightarrow \boldsymbol{\varepsilon x}$ is meant to include the reversal of external magnetic fields. Second, the unperturbed Fokker-Planck operator $\left.\mathrm{L}^{0}(\mathbf{x}) \equiv \mathrm{L}(\mathbf{x}, t)\right|_{\Delta=0}$ must obey the detailed balance condition [41]

$$
\begin{equation*}
\mathrm{L}^{0}(\mathbf{x}) p^{\mathrm{eq}}(\mathbf{x})=p^{\mathrm{eq}}(\mathbf{x}) \mathrm{L}^{0 \dagger}(\boldsymbol{\varepsilon} \mathbf{x}) \tag{32}
\end{equation*}
$$

for the canonical distribution (27), which uniquely satisfies

$$
\begin{equation*}
\mathrm{L}^{0}(\mathbf{x}) p^{\mathrm{eq}}(\mathbf{x})=0 \tag{33}
\end{equation*}
$$

The dagger showing up in Eq. (32), from here onwards, designates the adjoint of the respective operator. Note that, while in Eq. (33) the operator $L^{0}(\mathbf{x})$ acts on the function $p^{\mathrm{eq}}(\mathbf{x})$, Eq. (32) is to be read as an operator identity, which becomes meaningful when applied to a specific function of $\mathbf{x}$. Physically, the relation (32) means that, once the system has reached its equilibrium state, the rate of transitions from state $\mathbf{x}$ to state $\mathbf{x}^{\prime}$ is balanced by the rate of transitions in the reverse direction.

The equilibrium Fokker-Planck operator $L^{0}(\mathbf{x})$ can be naturally decomposed into a reversible and an irreversible contribution,

$$
\begin{align*}
& \mathrm{L}_{\mathrm{rev}}^{0}(\mathbf{x}) \equiv\left[\mathrm{L}^{0}(\mathbf{x})-\mathrm{L}^{0}(\boldsymbol{\varepsilon} \mathbf{x})\right] / 2  \tag{34}\\
& \mathrm{~L}_{\mathrm{irr}}^{0}(\mathbf{x}) \equiv\left[\mathrm{L}^{0}(\mathbf{x})+\mathrm{L}^{0}(\boldsymbol{\varepsilon} \mathbf{x})\right] / 2 \tag{35}
\end{align*}
$$

which are characterized by their respective behavior under time reversal. While the irreversible part accounts for dissipative effects induced by the presence of the heat bath, the reversible part describes the intrinsic coupling of the system's degrees of freedom, which is not directly affected by the fluctuating environment. Since this autonomous part of the dynamics should preserve the internal energy of the system, we have to impose the condition

$$
\begin{equation*}
\mathrm{L}_{\mathrm{rev}}^{0 \dagger}(\mathbf{x}) H_{0}(\mathbf{x})=0 \tag{36}
\end{equation*}
$$

We note that this consideration does not play a role in the overdamped limit, within which the entire time evolution of the system is effectively irreversible because of strongly dominating friction forces.

The notion of detailed balance cannot be immediately generalized to situations with external driving and timedependent temperature. However, in analogy with Eq. (33), the full Fokker-Planck operator $\mathrm{L}(\mathbf{x}, t)$ can still be characterized by the weaker property

$$
\begin{equation*}
\mathrm{L}(\mathbf{x}, t) \exp \left[-H(\mathbf{x}, t) /\left(k_{B} T(t)\right)\right]=0 \tag{37}
\end{equation*}
$$

which is naturally obeyed in the absence of nonconservative forces and guarantees that the system follows the correct thermal equilibrium state if the Hamiltonian and the temperature are varied quasistatically.

## 4. Finite-time kinetic coefficients

In the linear response regime, the Fokker-Planck operator $\mathrm{L}(t)$ showing up in Eq. (29) can be replaced by the expansion

$$
\begin{equation*}
\mathrm{L}(t) \equiv \mathrm{L}^{0}+\Delta H \mathrm{~L}^{H}(t)+\Delta T \mathrm{~L}^{T}(t)+\mathcal{O}\left(\Delta^{2}\right) \tag{38}
\end{equation*}
$$

where, for simplicity, from Eq. (38) onwards, we notationally suppress the dependence of any operator on $\mathbf{x}$, whenever there is no need to indicate it explicitly. The Fokker-Planck equation (29) can then be solved with due consideration of the boundary condition (6) by treating $\mathrm{L}^{H}(t)$ and $\mathrm{L}^{T}(t)$ as first-order perturbations. The result of this standard procedure [41,44] reads

$$
\begin{align*}
p^{\mathrm{c}}(\mathbf{x}, t)= & p^{\mathrm{eq}}(\mathbf{x})+\sum_{X=H, T} \Delta X \int_{0}^{\infty} d \tau e^{\mathrm{L}^{0} \tau} \mathrm{~L}^{X}(t-\tau) p^{\mathrm{eq}}(\mathbf{x}) \\
& +\mathcal{O}\left(\Delta^{2}\right) \tag{39}
\end{align*}
$$

After some algebra involving condition (37), which we relegate to Appendix A for convenience, this solution leads to the compact expression

$$
\begin{equation*}
L_{\alpha \beta}=L_{\alpha \beta}^{\mathrm{ad}}+\frac{1}{k_{B}} \int_{0}^{\infty} d \tau\left\langle\left\langle\delta \dot{g}_{\alpha}(0) ; \delta \dot{g}_{\beta}(-\tau)\right\rangle\right\rangle \tag{40}
\end{equation*}
$$

for the kinetic coefficients, where the generalized equilibrium correlation function is defined as

$$
\left\langle\left\langle A\left(t_{1}\right) ; B\left(t_{2}\right)\right\rangle\right\rangle \equiv \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} \begin{cases}A\left(\mathbf{x}, t_{1}+t\right) e^{\mathrm{L}^{0}\left(t_{1}-t_{2}\right)} B\left(\mathbf{x}, t_{2}+t\right) p^{\mathrm{eq}}(\mathbf{x}) & \text { for }\left(t_{1} \geq t_{2}\right)  \tag{41}\\ B\left(\mathbf{x}, t_{2}+t\right) e^{\mathrm{L}^{0}\left(t_{2}-t_{1}\right)} A\left(\mathbf{x}, t_{1}+t\right) p^{\mathrm{eq}}(\mathbf{x}) & \text { for }\left(t_{1}<t_{2}\right)\end{cases}
$$

for arbitrary quantities $A(\mathbf{x}, t)$ and $B(\mathbf{x}, t)$. We recall the definition (26) of the $\delta$ notation.

The expression (40) admits an illuminating physical interpretation. It shows that the kinetic coefficients of periodically driven systems can be decomposed into an adiabatic contribution independently identified in Eq. (24) and a finite-time correction, which has the form of an equilibrium correlation function. This result might therefore be regarded as a generalization of the well-established Green-Kubo relations, which relate linear transport coefficients such as electric or thermal conductivity to equilibrium correlation functions of the corresponding currents [44]. In our case, the role of the currents is played by the fluctuation variables $\delta \dot{g}_{\alpha}(\mathbf{x}, t)$, and the ensemble average is augmented by a temporal average over one operation cycle. We note that a similar expression has been obtained for the special case of the effective diffusion constant of a rocked inertial Brownian motor in Ref. [45].

## 5. Reciprocity relations

Time-reversal symmetry of microscopic dynamics appears as the detailed balance condition (32) on the level of the Fokker-Planck equation. By using this relation and the Green-Kubo-type formula (40), it is straightforward to derive the generalized reciprocity relation

$$
\begin{equation*}
L_{\alpha \beta}[H(\mathbf{x}, t), T(t), \mathbf{B}]=L_{\beta \alpha}[H(\mathbf{x},-t), T(-t),-\mathbf{B}] \tag{42}
\end{equation*}
$$

where the Onsager coefficients are considered as functionals of the time-dependent Hamiltonian and temperature and an external magnetic field B. The technical details of the derivation leading to the relation (42) can be found in Appendix B. Here, we emphasize that, although the setup of this paper differs significantly from the one Onsager dealt with in his pioneering work [12,13], the symmetry (42), which constitutes our second main result, and the original Onsager relations share microscopic reversibility
as the common physical origin. Since, in the presence of time-dependent driving, full time reversal especially includes reversal of the driving protocols, naturally, these reversed protocols show up in Eq. (42).

The symmetry (42) holds individually for both the adiabatic kinetic coefficients and the finite-time correction showing up in Eq. (40). Given the general relation (28), it follows that the $L_{\alpha \beta}^{\mathrm{ad}}$ must vanish if the driving protocols are symmetric under time reversal.

The additional relation

$$
\begin{equation*}
L_{\alpha \beta}\left[\gamma_{w}(t), \gamma_{q}(t), \mathbf{B}\right]=L_{\beta \alpha}\left[\gamma_{q}(t), \gamma_{w}(t),-\mathbf{B}\right] \tag{43}
\end{equation*}
$$

can be proven if the driving $g_{w}(\mathbf{x}, t)$ introduced in Eq. (1) factorizes according to

$$
\begin{equation*}
g_{w}(\mathbf{x}, t)=g_{w}(\mathbf{x}) \gamma_{w}(t) \tag{44}
\end{equation*}
$$

Hence, the off-diagonal kinetic coefficients change place if the magnetic field is reversed and the respective protocols determining the time dependence of the Hamiltonian and the temperature are interchanged. This symmetry does not involve the reversed protocols. It is, however, less universal than Eq. (42) since it requires the special structure (44) (see Appendix B for details).

## III. CYCLIC STOCHASTIC HEAT ENGINES IN LINEAR RESPONSE

As a key application of our new approach, we discuss the performance of stochastic heat engines.

## A. Power and efficiency

The two main benchmark parameters here are, first, the average power output per operation cycle,
$P \equiv-\frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x} \dot{H}(\mathbf{x}, t) p^{\mathrm{c}}(\mathbf{x}, t)=-T_{\mathrm{c}} \mathcal{F}_{w} J_{w}$,
and, second, the efficiency

$$
\begin{equation*}
\eta \equiv P / J_{q}=-T_{\mathrm{c}} \mathcal{F}_{w} J_{w} / J_{q} \tag{46}
\end{equation*}
$$

which is bounded by the Carnot value $\eta_{\mathrm{C}}=1-T_{\mathrm{c}} / T_{\mathrm{h}}$ as a direct consequence of the second law $\dot{S} \geq 0$. The latter figure, which is naturally suggested by the representation (11) of the entropy production per cycle, should be regarded as a generalization of the conventional thermodynamic efficiency defined for a heat engine operating between two reservoirs of respectively constant temperature. Our formalism includes this scenario as the special case where $\gamma_{q}(t)$ is chosen as a step function,

$$
\gamma_{q}(t)= \begin{cases}1 & \text { for } 0 \leq t<\mathcal{T}_{1}  \tag{47}\\ 0 & \text { for } \mathcal{T}_{1} \leq t<\mathcal{T}\end{cases}
$$

with $0<\mathcal{T}_{1}<\mathcal{T}$ such that the system is in contact with the hot temperature $T_{\mathrm{h}}$ in the first part of the cycle and the cold temperature $T_{\mathrm{c}}$ in the second one.

Under linear response conditions, which we assume for the rest of this section, the fluxes $J_{\alpha}$ can be eliminated using Eq. (17) such that the expressions (45) and (46) reduce to

$$
\begin{equation*}
P=-T_{\mathrm{c}} \mathcal{F}_{w}\left(L_{w w} \mathcal{F}_{w}+L_{w q} \mathcal{F}_{q}\right) \tag{48}
\end{equation*}
$$

and

$$
\begin{equation*}
\eta=-\frac{T_{\mathrm{c}} \mathcal{F}_{w}\left(L_{w w} \mathcal{F}_{w}+L_{w q} \mathcal{F}_{q}\right)}{L_{q w} \mathcal{F}_{w}+L_{q q} \mathcal{F}_{q}} \tag{49}
\end{equation*}
$$

respectively. Clearly, these figures are crucially determined by the kinetic coefficients $L_{\alpha \beta}$. In contrast to the thermoelectric case, where the reciprocity relation $L_{\alpha \beta}=L_{\beta \alpha}$ holds without magnetic fields, the analysis of the preceding section has revealed that for cyclic heat engines, this symmetry is typically broken if the driving protocols are not invariant under time reversal. As pointed out by Benenti et al. [31], a nonsymmetric matrix of kinetic coefficients leads to profound consequences for the performance of thermoelectric devices including the option of Carnot efficiency at finite power.

These results apply similarly to the systems considered here since our theoretical framework is structurally equivalent to the standard theory of linear irreversible thermodynamics used as a starting point in Ref. [31]. To demonstrate this correspondence explicitly, following Ref. [31], we define the dimensionless parameters

$$
\begin{align*}
& x \equiv \frac{L_{w q}}{L_{q w}} \quad \text { and } \\
& y \equiv \frac{L_{w q} L_{q w}}{L_{w w} L_{q q}-L_{w q} L_{q w}}, \tag{50}
\end{align*}
$$

which, because of the second law (21), are related by the inequalities

$$
\begin{equation*}
h(x) \leq y \leq 0 \quad \text { for } x<0, \quad 0 \leq y \leq h(x) \quad \text { for } x \geq 0 \tag{51}
\end{equation*}
$$

with

$$
\begin{equation*}
h(x) \equiv \frac{4 x}{(x-1)^{2}} \tag{52}
\end{equation*}
$$

By optimizing Eqs. (48) and (49), respectively, as functions of $\mathcal{F}_{w}$, the expressions

$$
\begin{equation*}
\eta_{\max }(x, y) \equiv \eta_{\mathrm{C}} x \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1} \tag{53}
\end{equation*}
$$



FIG. 2. Plots of the maximum power (57) in units of $P_{0} \equiv$ $T_{\mathrm{c}} \mathcal{F}_{q}^{2} L_{q q}$ as a function of the normalized efficiency $\bar{\eta} \equiv \eta / \eta_{\mathrm{C}}$ for selected values of the asymmetry parameter $x \geq 1$ in the upper and $x<-1$ in the lower panel. For $x \rightarrow \pm \infty$, convergence to $P / P_{0}=\bar{\eta}$ is observed. The dotted black lines correspond to the maxima of Eq. (57) for $0 \leq x<\infty$ in the first and $-\infty<x<-1$ in the second plot, thus indicating the relation between maximum power and efficiency at maximum power. The apparent divergence for negative $x$ occurs in the limit $x \rightarrow-1$ [48].
for maximum efficiency and

$$
\begin{equation*}
\eta^{*}(x, y)=\eta_{\mathrm{C}} \frac{x y}{4+2 y} \tag{54}
\end{equation*}
$$

for efficiency at maximum power [30] are obtained, where $\eta_{\mathrm{C}} \approx \Delta T / T_{\mathrm{c}}=T_{\mathrm{c}} \mathcal{F}_{q}$ denotes the Carnot efficiency in the linear regime. For $y=h(x)$ and $|x| \geq 0$, the maximum efficiency equals $\eta_{\mathrm{C}}$ and the efficiency at maximum power can exceed the Curzon-Ahlborn value $\eta_{\mathrm{C}} / 2$ [27-30,46,47], reaching even $\eta_{\mathrm{C}}$ in the limit $x \rightarrow \pm \infty$.

For a quantitative assessment of the relation between power and efficiency, following Ref. [39], we consider the maximum power at a given efficiency,

$$
\begin{align*}
P(\eta, x, y)= & T_{\mathrm{c}} \mathcal{F}_{q}^{2} L_{q q} \bar{\eta}\left(\frac{x(2+y)-y \bar{\eta}}{2 x(1+y)}\right. \\
& \left.+\sqrt{\frac{y^{2}(x+\bar{\eta})^{2}}{4 x^{2}(1+y)^{2}}-\frac{y \bar{\eta}}{x(1+y)}}\right) \tag{55}
\end{align*}
$$

as a joint benchmark parameter, which is found by eliminating $\mathcal{F}_{w}$ in Eq. (45) in favor of

$$
\begin{equation*}
\bar{\eta} \equiv \eta / \eta_{\mathrm{C}} \tag{56}
\end{equation*}
$$

using Eq. (49). To ensure that the Carnot value $\eta_{C}$ is included in the range of accessible efficiencies, $y$ must be replaced by its bound $h(x)$ in Eq. (55). The resulting function

$$
\begin{equation*}
P(\eta, x) \equiv P(\eta, x, h(x)) \tag{57}
\end{equation*}
$$

is plotted in Fig. 2. While $P(\eta, x)$ reduces to

$$
\begin{equation*}
P(\eta, 1)=T_{\mathrm{c}} \mathcal{F}_{q}^{2} L_{q q} \bar{\eta}(1-\bar{\eta}) \tag{58}
\end{equation*}
$$

in the symmetric case $x=1$ and thus vanishes linearly in the limit $\eta \rightarrow \eta_{\mathrm{C}}$, strikingly, we observe that Carnot efficiency might be reached at finite power [48],

$$
\begin{equation*}
P\left(\eta_{\mathrm{C}}, x\right)=T_{\mathrm{c}} \mathcal{F}_{q}^{2} L_{q q} \frac{x-1}{x+1} \quad \text { for }|x|>1 \tag{59}
\end{equation*}
$$

This result is a priori surprising since this analysis has fully incorporated the constraints imposed by the second law.

## B. A new constraint

We now prove the existence of an additional constraint on the kinetic coefficients (19), which, so far, has been missing in our considerations. To this end, we introduce the symmetric matrix

$$
\mathrm{A} \equiv\left(\begin{array}{ccc}
N_{q q} & L_{q w} & L_{q q}  \tag{60}\\
L_{q w} & L_{w w} & \frac{1}{2}\left(L_{w q}+L_{q w}\right) \\
L_{q q} & \frac{1}{2}\left(L_{w q}+L_{q w}\right) & L_{q q}
\end{array}\right)
$$

where

$$
\begin{equation*}
N_{q q} \equiv-\frac{1}{k_{B}}\left\langle\left\langle\delta g_{q} \mathrm{~L}^{0 \dagger} \delta g_{q}\right\rangle\right\rangle \tag{61}
\end{equation*}
$$

plays the role of a normalization constant and $\langle\langle\bullet\rangle\rangle$ was defined in Eq. (25). The matrix $A$ has the nontrivial property of being positive semidefinite such that the determinant of any of its principal submatrices must be non-negative, as we show in Appendix C by using only the rather general assumptions of Sec. II B.

Two important implications follow immediately from this insight. First, by taking the determinant of the lower-right $2 \times 2$ submatrix, we recover the inequality (21), which we inferred from the second law on the phenomenological level and now have proven explicitly. Second, by evaluating the determinant of $\mathbb{A}$, we get the new constraint

$$
\begin{align*}
L_{q q} & \leq N_{q q} \frac{L_{w w} L_{q q}-\left(L_{w q}+L_{q w}\right)^{2} / 4}{L_{w w} L_{q q}-L_{w q} L_{q w}}  \tag{62}\\
& =N_{q q}[1-y / h(x)] \tag{63}
\end{align*}
$$

which, in contrast to the bare second law, leads to a bound on power. Specifically, this bound is found by bounding $L_{q q}$ in Eq. (55) using Eq. (63) and then maximizing the resulting function with respect to $y$ [39]. This procedure yields the simple result

$$
P(\eta, x) \leq \hat{P}(\eta, x) \equiv 4 \bar{P}_{0} \begin{cases}\bar{\eta}(1-\bar{\eta}) & \text { for }|x| \geq 1  \tag{64}\\ \bar{\eta}-\bar{\eta}^{2} / x^{2} & \text { for }|x|<1\end{cases}
$$

where we define the standard power

$$
\begin{equation*}
\bar{P}_{0} \equiv T_{\mathrm{c}} \mathcal{F}_{q}^{2} N_{q q} / 4 \tag{65}
\end{equation*}
$$

and $y$ becomes

$$
\begin{array}{ll}
y^{*}(x, \eta)=\frac{4 x \bar{\eta}}{(x-1)(1+x-2 \bar{\eta})} \quad \text { for }|x| \geq 1 \\
y^{*}(x, \eta)=\frac{4 \bar{\eta}}{x-x^{3}-2 \bar{\eta}+2 x \bar{\eta}} \quad \text { for }|x|<1 \tag{66}
\end{array}
$$

through the optimization. Remarkably, for any $|x| \geq 1$ the bound (64), which is our third main result, restores the quadratic relation between power and efficiency (58), which we found in our first analysis by not invoking the new bound (63) only for the symmetric case $x=1$. Consequently, we have shown that, in the linear response regime, the power of any cyclic heat engine comprised of our theoretical framework must vanish at least linearly as its efficiency approaches the Carnot value. We emphasize that this quite natural result can neither be derived from the laws of thermodynamics nor from micro-reversibility, which appears in the form of the reciprocity relation (42). Instead, it relies on the additional constraint (62), which is beyond both of these principles.

## IV. AN ILLUSTRATIVE EXAMPLE

## A. Model and kinetic coefficients

A particularly simple setup for a stochastic heat engine consists of a Brownian particle in one spatial dimension confined in a harmonic potential of variable strength $\kappa(t)$ and immersed in a heat bath of time-dependent temperature $T(t)$ as schematically shown in Fig. 3. Originally proposed in Ref. [14], this model has recently been realized in a remarkable experiment [2] and can be used to illustrate various aspects of stochastic thermodynamics like the role of feedback [49,50] and shortcuts to adiabaticity [51].

Here, by applying our general theory developed in the last sections, we calculate the kinetic coefficients for this stochastic heat engine and optimize the protocol $\kappa(t)$ controlling the trap strength to obtain maximum power for a given efficiency.

In the overdamped limit, because of the absence of kinetic energy, the Hamiltonian of the system


FIG. 3. Operation cycle of a Brownian heat engine. The vertical axis corresponds to the normalized time-dependent strength of the harmonic trap in units of $\wp \equiv \kappa(t) / \kappa_{0}$, the horizontal axis to the normalized width $\mathcal{V} \equiv\left\langle x^{2}\right\rangle /\left(2 x_{0}^{2}\right)$ of the distribution function. This plot is analogous to the pressure volume diagram of a macroscopic heat engine such that the area encircled by the colored lines quantifies the work extracted per operation cycle. Specifically, the plots were obtained using the protocols (73) and (80) for different values of the shape parameter $d, 2 \mu \kappa_{0} \mathcal{T}=1$, $\eta_{\mathrm{C}}=T_{\mathrm{c}} \mathcal{F}_{q}=1 / 10$ and $\bar{\eta}=1 / 2$. The small graphics show sketches of the potential (gray line) and the phase-space distribution, whose color reflects the temperature of the heat bath, at the respective edges of the cycle. For further explanations, see Sec. IV.

$$
\begin{align*}
H(x, t) & =H_{0}(x)+\Delta H g_{w}(x, t) \quad \text { with } \\
H_{0}(x) & \equiv \frac{\kappa_{0}}{2} x^{2} \\
\Delta H & \equiv \kappa x_{0}^{2} \\
g_{w}(x, t) & \equiv \frac{x^{2}}{2 x_{0}^{2}} \gamma_{w}(t) \tag{67}
\end{align*}
$$

depends only on the position $x$ of the particle. Here, $\kappa_{0}$ is the equilibrium strength of the trap, $\kappa$ quantifies the strength of the time-dependent driving, $\gamma_{w}(t)$ denotes the driving protocol, and $x_{0} \equiv \sqrt{2 k_{B} T_{\mathrm{c}} / \kappa_{0}}$ is the characteristic length scale of the system. The time evolution of the probability density $p(x, t)$ for finding the particle at the position $x$ is generated by the Fokker-Planck operator

$$
\begin{equation*}
\mathrm{L}(t) \equiv \mu\left[\kappa_{0}+\kappa \gamma_{w}(t)\right] \partial_{x} x+\mu k_{B} T(t) \partial_{x}^{2} \tag{68}
\end{equation*}
$$

which, in equilibrium, reduces to

$$
\begin{equation*}
\mathrm{L}^{0} \equiv \mu \kappa_{0} \partial_{x} x+\mu k_{B} T_{\mathrm{c}} \partial_{x}^{2} \tag{69}
\end{equation*}
$$

Here, $\mu$ denotes the mobility, and the temperature $T(t) \equiv$ $T_{\mathrm{c}} T_{\mathrm{h}} /\left[T_{\mathrm{h}}-\Delta T \gamma_{q}(t)\right]$ oscillates between the cold and the hot levels $T_{\mathrm{c}}$ and $T_{\mathrm{h}} \equiv T_{\mathrm{c}}+\Delta T$. The equilibrium fluctuations in Eq. (40) read

$$
\begin{equation*}
\delta g_{\alpha}(x, t)=\gamma_{\alpha}(t) \kappa_{0} \xi_{\alpha}\left(x^{2}-k_{B} T_{\mathrm{c}} / \kappa_{0}\right) \tag{70}
\end{equation*}
$$

with

$$
\begin{equation*}
\xi_{w} \equiv 1 /\left(4 k_{B} T_{\mathrm{c}}\right) \quad \text { and } \quad \xi_{q} \equiv-1 / 2 \tag{71}
\end{equation*}
$$

Formula (40) can be easily evaluated by using the detailed balance relation (32) to transform $\mathrm{L}^{0}$ into $\mathrm{L}^{0 \dagger}$ since it is readily seen that the function $x^{2}-k_{B} T_{\mathrm{c}} / \kappa_{0}$ is a right eigenvector of $\mathrm{L}^{0 \dagger}$ with corresponding eigenvalue $-2 \mu \kappa_{0}$. The resulting kinetic coefficients

$$
\begin{align*}
L_{\alpha \beta}= & -\frac{2 k_{B} T_{\mathrm{c}}^{2} \xi_{\alpha} \xi_{\beta}}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t\left(\dot{\gamma}_{\alpha}(t) \gamma_{\beta}(t)\right. \\
& \left.-\int_{0}^{\infty} d \tau \dot{\gamma}_{\alpha}(t) \dot{\gamma}_{\beta}(t-\tau) e^{-2 \mu \kappa_{0} \tau}\right) \tag{72}
\end{align*}
$$

are functionals of the protocols $\gamma_{\alpha}(t)$. Note that, besides the general reciprocity relation (42), these coefficients also satisfy the special symmetry relation (43) since the factorization condition (44) is fulfilled in the example discussed here.

## B. Optimization

The optimal protocol $\gamma_{w}^{*}(t, \eta)$ for the strength of the harmonic trap for a given time dependence of temperature $\gamma_{q}(t)$ maximizes the power output at fixed efficiency $\eta$. It is determined by the variational condition

$$
\begin{equation*}
\left.0 \stackrel{!}{=} \frac{\delta}{\delta \gamma_{w}(t)} P\left[\gamma_{w}(t), \gamma_{q}(t)\right]\right|_{P / J_{q} \stackrel{!}{=}}, \tag{73}
\end{equation*}
$$

where the power $P$ and the heat flux $J_{q}$ are regarded as functionals of $\gamma_{w}(t)$ and $\gamma_{q}(t)$. As we show in Appendix D, this constrained optimization problem has the general solution

$$
\begin{align*}
\gamma_{w}^{*}(t, \eta)= & \frac{\kappa_{0} \eta_{\mathrm{C}}}{\kappa}\left(\bar{\eta} \gamma_{q}(t)-2(1-\bar{\eta}) \mu \kappa_{0} \int_{0}^{t} d \tau\left[\gamma_{q}(\tau)-\overline{\gamma_{q}}\right]\right) \\
& +\gamma_{0} \tag{74}
\end{align*}
$$

for $0 \leq t \leq \mathcal{T}$, where we used the abbreviation (56), the definition

$$
\begin{equation*}
\bar{\gamma}_{q} \equiv \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \gamma_{q}(t) \tag{75}
\end{equation*}
$$

and $\gamma_{0}$ as an arbitrary constant. Using this protocol, the maximum power
$P_{\max }(\eta)=\frac{k_{B} T_{\mathrm{c}}^{3} \mathcal{F}_{q}^{2} \mu \kappa_{0}}{\mathcal{T}} \bar{\eta}(1-\bar{\eta}) \int_{0}^{\mathcal{T}} d t\left(\gamma_{q}(t)-\bar{\gamma}_{q}\right)^{2}$
can be extracted per operation cycle at efficiency $\eta$.

## C. Comparison with general bound

In order to compare this result with the general bound (64), we evaluate the normalization constant

$$
\begin{equation*}
N_{q q}=\frac{k_{B} T_{\mathrm{c}}^{2} \mu \kappa_{0}}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \gamma_{q}^{2}(t) \tag{77}
\end{equation*}
$$

defined in Eq. (61) and rewrite Eq. (76) as

$$
\begin{equation*}
P_{\max }(\eta)=4 \psi \bar{P}_{0} \bar{\eta}(1-\bar{\eta}) \tag{78}
\end{equation*}
$$

where $\bar{P}_{0}$ is the standard power introduced in Eq. (64). The dimensionless factor

$$
\begin{equation*}
0 \leq \psi \equiv \frac{\int_{0}^{\mathcal{T}} d t\left[\gamma_{q}(t)-\bar{\gamma}_{q}\right]^{2}}{\int_{0}^{\mathcal{T}} d t \gamma_{q}^{2}(t)} \leq 1 \tag{79}
\end{equation*}
$$

quantifies how close the maximum power found in the optimization comes to the general bound (64). Since $0 \leq \gamma_{q}(t) \leq 1$, it is reached only for $\bar{\gamma}_{q} \rightarrow 0$. This limit, however, requires $\gamma_{q}(t) \rightarrow 0$ for any $t$ and thus, inevitably, leads to vanishing absolute power.

For an illustration of this issue, we chose $\gamma_{q}(t)$ as the step function (47) such that the system is alternately in contact with a hot and a cold bath, respectively, during the time intervals $\mathcal{T}_{1}$ and $\mathcal{T}-\mathcal{T}_{1}$. We then find $\psi=1-\mathcal{T}_{1} / \mathcal{T}$ and $P_{0} \sim \mathcal{T}_{1} / \mathcal{T}$. Thus, as $\mathcal{T}_{1}$ is decreased, $\psi$ comes arbitrarily close to 1 and $P_{0}$ decays linearly to zero. This example shows that our bound is asymptotically tight.

A particular advantage of our approach is that it allows us to treat situations with a continuously varying temperature of the environment on equal footing with the scenario proposed in Ref. [14], which involves instantaneous switchings between a hot and a cold reservoir. In order to illustrate this feature, we consider the specific choice

$$
\begin{equation*}
\gamma_{q}(t, d) \equiv \frac{\sqrt{1+d} \sin [2 \pi t / \mathcal{T}]}{2 \sqrt{\sin ^{2}[2 \pi t / \mathcal{T}]+d}}+\frac{1}{2} \tag{80}
\end{equation*}
$$

for the protocol $\gamma_{q}(t)$, which, in the linear response regime, is proportional to the temperature $T(t)$. The function (80), which interpolates between a step function $(d \rightarrow 0)$ and a simple sine $(d \rightarrow \infty)$ [52], is plotted together with the corresponding optimal protocol $\gamma_{w}^{*}(t, \eta, d)$ [53] in Fig. 4. We find that, for $d=0$, this protocol shows two sudden jumps occurring simultaneously with the instantaneous changes of the bath temperature. Such discontinuities were shown to be typical for thermodynamically optimized finite-time protocols connecting two equilibrium states


FIG. 4. Plots of the temperature protocol $\gamma_{q}(t, d)$ defined in Eq. (80) (dashed lines) and the corresponding optimal protocol $\gamma_{w}^{*}(t, \eta, d)$ for the trap strength (solid lines) obtained from Eq. (74) for four different values of the parameter $d$ as functions of $t / \mathcal{T}$ [53]. For all plots, we have set $2 \mu \kappa_{0} \mathcal{T}=1$ and $\bar{\eta}=1 / 2$. Additionally, the optimal protocol $\gamma_{w}^{*}(t)$ has been rescaled by the dimensionless factor $\kappa_{0} \eta_{\mathrm{C}} / \kappa$.
[54]. Since, here, we are concerned with periodic states generated by permanent driving rather than a transient process with equilibrium boundary conditions, it is, however, not surprising that both the temperature and the trap strength protocol become continuous as the shape parameter $d$ is increased.

For the protocols (73) and (80), the parameter $\psi$ becomes

$$
\begin{equation*}
\psi=\frac{1+d}{2(1+d)+\sqrt{d(1+d)}} \tag{81}
\end{equation*}
$$

This function decays monotonically from $1 / 2$ for $d=0$ to $1 / 3$ for $d \rightarrow \infty$. Consequently, $\psi$ cannot reach its maximum 1 within the class of protocols (80). This limitation can be understood from the argument given below Eq. (79) since, for any $d$, we have $\bar{\gamma}_{q}=1 / 2$.

The standard power $P_{0}$ is proportional to the function $2+d-\sqrt{d(1+d)}$, which decays monotonically from 2 to $3 / 2$ as $d$ increases from 0 to infinity. Thus, $P_{0}$ exhibits the same qualitative dependence on the shape parameter $d$ as the efficiency. We can therefore conclude that, at least within the model considered here, a steeply rising and falling temperature performs better than a smoothly changing one.

## V. CONCLUDING PERSPECTIVES

In this work, we have demonstrated that nonequilibrium periodic states, which emerge naturally in periodically driven systems, can be endowed with the universal structure of irreversible thermodynamics. Moreover, by using a quite general stochastic approach, we have proven the generalized reciprocity relation (42) for the kinetic coefficients characterizing the linear response regime.

Our new framework is particularly useful for a systematic study of the performance of cyclic heat engines. Within
the linear regime, bounding the power of these machines in such a way that the rather peculiar option of Carnot efficiency at finite power is ruled out requires the new relation (62). This constraint is beyond the laws of thermodynamics and the principle of microscopic reversibility and has been proven here for the first time on a general level. Remarkably, up to the normalization factor, an identical bound has been discovered only recently in a numerical analysis of a particular class of thermoelectric heat engines [39]. Whether this intriguing similarity suggests the existence of a so-far-undiscovered universal principle that applies to periodic as well as to steady states leading to a bound on power for any type of heat engine that operates in the linear regime remains an exciting topic for future research.

A promising starting point for investigations in this direction might be found in the Green-Kubo relations, which follow from first principles and provide general expressions for the conventional kinetic coefficients in terms of equilibrium correlation functions [44]. Using a Fokker-Planck approach, we have shown that an analogous representation for the kinetic coefficients exists in periodically driven systems. The quantities related by the relevant correlation functions are, however, well defined irrespective of specific dynamics governing the time evolution of the phase-space density. It might therefore be possible to also obtain Hamiltonian-based expressions for the periodic kinetic coefficients introduced in this work. Finding a proper way to take the time dependence of temperature into account is arguably the major challenge here.

This problem also prevents an immediate extension of our formalism to the quantum realm. While the first part of our analysis, the identification of proper fluxes and affinities, carries over to quantum mechanics line by line, it is not clear at the moment whether the constraints on the kinetic coefficients obtained here classically can be likewise transferred or properly generalized. This topic appears all the more urgent in the light of recent developments [5,55,56], showing that the emerging field of quantum thermodynamics nowadays comes within the range of experiments.

## ACKNOWLEDGMENTS

K. B. acknowledges support from the German Academic Exchange Service (DAAD). K. S. was supported by JSPS (No. 26400404) and MEXT (No. 25103003). This work was supported by the German Research Foundation (DFG) within the funding programme Open Access Publishing.

## APPENDIX A: DERIVATION OF EXPRESSION (40) FOR THE ONSAGER COEFFICIENTS

For an expression of the kinetic coefficients (19) depending only on equilibrium quantities, the perturbations $\mathrm{L}^{X}(t)$ showing up in the linear response solution (39) have to be eliminated. To this end, we invoke the property (37) of the
full Fokker-Planck operator. Substituting Eq. (38) into Eq. (37), expanding the exponential in $\Delta H$ and $\Delta T$, and collecting linear-order terms provides us with the relations

$$
\begin{align*}
\Delta H \mathrm{~L}^{H}(t) p^{\mathrm{eq}}(\mathbf{x}) & =\mathcal{F}_{w} \mathrm{~L}^{0} g_{w}(\mathbf{x}, t) p^{\mathrm{eq}}(\mathbf{x}) / k_{B} \\
\Delta T \mathrm{~L}^{T}(t) p^{\mathrm{eq}}(\mathbf{x}) & =\mathcal{F}_{q} \mathrm{~L}^{0} g_{q}(\mathbf{x}, t) p^{\mathrm{eq}}(\mathbf{x}) / k_{B} \tag{A1}
\end{align*}
$$

where we used the definition (16). Up to corrections of order $\Delta^{2}$, the periodic distribution $p^{\mathrm{c}}(\mathbf{x}, t)$ can thus be rewritten as

$$
\begin{align*}
p^{\mathrm{c}}(\mathbf{x}, t)= & p^{\mathrm{eq}}(\mathbf{x})+\sum_{\alpha=w, q} \frac{\mathcal{F}_{\alpha}}{k_{B}} \int_{0}^{\infty} d \tau e^{\mathrm{L}^{\mathrm{o}} \tau} \mathrm{~L}^{0} g_{\alpha}(\mathbf{x}, t-\tau) p^{\mathrm{eq}}(\mathbf{x})  \tag{A2}\\
= & p^{\mathrm{eq}}(\mathbf{x})+\sum_{\alpha=w, q} \frac{\mathcal{F}_{\alpha}}{k_{B}} \int_{0}^{\infty} d \tau e^{\mathrm{L}^{0} \tau} \mathrm{~L}^{0} \delta g_{\alpha}(\mathbf{x}, t-\tau) p^{\mathrm{eq}}(\mathbf{x})  \tag{A3}\\
= & p^{\mathrm{eq}}(\mathbf{x})-\sum_{\alpha=w, q} \frac{\mathcal{F}_{\alpha}}{k_{B}}\left(\delta g_{\alpha}(\mathbf{x}, t) p^{\mathrm{eq}}(\mathbf{x})\right. \\
& \left.-\int_{0}^{\infty} d \tau e^{\mathrm{L}^{0} \tau} \delta \dot{g}_{\alpha}(\mathbf{x}, t-\tau) p^{\mathrm{eq}}(\mathbf{x})\right) . \tag{A4}
\end{align*}
$$

In the second line, we replaced $g_{\alpha}(\mathbf{x}, t)$ with its equilibrium fluctuation defined in Eq. (26). This modification does not alter the right-hand side of Eq. (A2) since $\mathrm{L}^{0} p^{\mathrm{eq}}(\mathbf{x})=0$. However, it ensures that the function, on which the exponential operator acts in the third line, which was obtained by an integration by parts with respect to $t$, has no overlap with the null space of $\mathrm{L}^{0}$ and thus the integral with an infinite upper bound is well defined. Note that the upper boundary term vanishes since the operator $\mathrm{L}^{0}$ is nonpositive [41]. Inserting Eq. (A2) into Eqs. (12) and (15) yields

$$
\begin{equation*}
L_{\alpha \beta}=-\frac{1}{k_{B}}\left\langle\left\langle\dot{g}_{\alpha} \delta g_{\beta}\right\rangle\right\rangle+\frac{1}{k_{B}} \int_{0}^{\infty} d \tau\left\langle\left\langle\dot{g}_{\alpha}(0) ; \delta \dot{g}_{\beta}(-\tau)\right\rangle\right\rangle \tag{A5}
\end{equation*}
$$

Herein, obviously, $\dot{g}_{\alpha}(\mathbf{x}, t)$ can be replaced by its equilibrium fluctuation $\delta \dot{g}_{\alpha}(\mathbf{x}, t)$ in the first term. Since any constant lies in the left null space of $\mathrm{L}^{0}$ and, hence, is orthogonal to the function $e^{\mathrm{L}^{0} \tau} \delta \dot{g}_{\alpha}(\mathbf{x}, t-\tau) p^{\mathrm{eq}}(\mathbf{x})$, the same replacement can be carried out in the second term without leading to additional contributions such that Eq. (40) is, finally, obtained.

## APPENDIX B: RECIPROCITY RELATIONS

In this appendix, we establish the reciprocity relations (42) and (43). To this end, we first recall formula (40), which becomes

$$
\begin{align*}
L_{\alpha \beta}[ & H(\mathbf{x}, t), T(t), \mathbf{B}] \\
= & -\frac{1}{k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x}\left(\delta \dot{g}_{\alpha}(\mathbf{x}, t) \delta g_{\beta}(\mathbf{x}, t) p^{\mathrm{eq}}(\mathbf{x})\right. \\
& \left.+\int_{0}^{\infty} d \tau \delta \dot{g}_{\alpha}(\mathbf{x}, t) e^{\mathrm{L}^{0} \tau} \delta \dot{g}_{\beta}(\mathbf{x}, t-\tau) p^{\mathrm{eq}}(\mathbf{x})\right), \tag{B1}
\end{align*}
$$

using the definitions (25) and (41). By applying the detailed balance relation (32) and changing the integration variable $t$ according to $t \rightarrow \mathcal{T}-t$, this expression can be transformed to

$$
\begin{align*}
L_{\alpha \beta} & {[H(\mathbf{x}, t), T(t), \mathbf{B}] } \\
= & -\frac{1}{k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x}\left(-\delta \dot{g}_{\alpha}(\mathbf{x},-t) \delta g_{\beta}(\mathbf{x},-t) p^{\mathrm{eq}}(\mathbf{x})\right. \\
& \left.+\int_{0}^{\infty} d \tau \delta \dot{g}_{\beta}(\mathbf{x},-t) e^{\tilde{L}^{0} \tau} \delta \dot{g}_{\alpha}(\mathbf{x}, \tau-t) p^{\mathrm{eq}}(\mathbf{x})\right), \tag{B2}
\end{align*}
$$

where we introduced the shorthand notation $\tilde{L}^{0} \equiv \mathrm{~L}^{0}(\boldsymbol{\varepsilon x})$. Furthermore, to transfer the variable $\tau$ from the argument of $\delta \dot{g}_{\beta}$ in Eq. (B1) to the argument of $\delta \dot{g}_{\alpha}$ in Eq. (B2), we used the identity

$$
\begin{align*}
& \int_{0}^{\mathcal{T}} d t a(t) b(t-\tau) \\
&= \int_{-\tau}^{\mathcal{T}-\tau} d t a(t+\tau) b(t) \\
&= \int_{0}^{\mathcal{T}} d t a(t+\tau) b(t)+\int_{-\tau}^{0} d t a(t+\tau) b(t) \\
&-\int_{\mathcal{T}-\tau}^{\mathcal{T}} d t a(t+\tau) b(t)=\int_{0}^{\mathcal{T}} d t a(t+\tau) b(t) \tag{B3}
\end{align*}
$$

which holds for any two $\mathcal{T}$-periodic functions $a(t)$ and $b(t)$. Finally, we reverse the magnetic field as well as the driving protocols and apply the change of integration variables $\mathbf{x} \rightarrow \boldsymbol{\varepsilon x}$, whose Jacobian is 1 . By exploiting the symmetry $\delta g_{\alpha}(\mathbf{\varepsilon x}, t)=\delta g_{\alpha}(\mathbf{x}, t)$, which follows from condition (31), and carrying out one integration by parts with respect to $t$ in the first summand, we obtain

$$
\begin{align*}
L_{\alpha \beta} & {[H(\mathbf{x},-t), T(-t),-\mathbf{B}] } \\
= & -\frac{1}{k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x}\left(\delta \dot{g}_{\beta}(\mathbf{x}, t) \delta g_{\alpha}(\mathbf{x}, t) p^{\mathrm{eq}}(\mathbf{x})\right. \\
& \left.+\int_{0}^{\infty} d \tau \delta \dot{g}_{\beta}(\mathbf{x}, t) e^{\mathrm{L}^{0} \tau} \delta \dot{g}_{\alpha}(\mathbf{x}, t-\tau) p^{\mathrm{eq}}(\mathbf{x})\right)  \tag{B4}\\
= & L_{\beta \alpha}[H(\mathbf{x}, t), T(t), \mathbf{B}], \tag{B5}
\end{align*}
$$

thus completing the proof of the reciprocity relation (42).
We now turn to the special case where the function $g_{w}(\mathbf{x}, t)$ can be separated in the form

$$
\begin{equation*}
g_{w}(\mathbf{x}, t)=g_{w}(\mathbf{x}) \gamma_{w}(t) \tag{B6}
\end{equation*}
$$

Plugging this expression into Eq. (B1) and invoking the definition $g_{q}(\mathbf{x}) \equiv-H_{0}(\mathbf{x})$ yields the expression

$$
\begin{align*}
L_{\alpha \beta} & {\left[\gamma_{w}(t), \gamma_{q}(t), \mathbf{B}\right] } \\
= & -\frac{1}{k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x}\left(\dot{\gamma}_{\alpha}(t) \gamma_{\beta}(t) \delta g_{\alpha}(\mathbf{x}) \delta g_{\beta}(\mathbf{x}) p^{\mathrm{eq}}(\mathbf{x})\right. \\
& \left.+\int_{0}^{\infty} d \tau \dot{\gamma}_{\alpha}(t) \dot{\gamma}_{\beta}(t-\tau) \delta g_{\alpha}(\mathbf{x}) e^{\mathrm{L}^{0} \tau} \delta g_{\beta}(\mathbf{x}) p^{\mathrm{eq}}(\mathbf{x})\right), \tag{B7}
\end{align*}
$$

which, by virtue of the detailed balance relation (32), equals

$$
\begin{align*}
L_{\alpha \beta} & {\left[\gamma_{w}(t), \gamma_{q}(t), \mathbf{B}\right] } \\
= & -\frac{1}{k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int d^{n} \mathbf{x}\left(\dot{\gamma}_{\alpha}(t) \gamma_{\beta}(t) \delta g_{\alpha}(\mathbf{x}) \delta g_{\beta}(\mathbf{x}) p^{\mathrm{eq}}(\mathbf{x})\right. \\
& \left.+\int_{0}^{\infty} d \tau \dot{\gamma}_{\alpha}(t) \dot{\gamma}_{\beta}(t-\tau) \delta g_{\beta}(\mathbf{x}) e^{\tilde{L}^{0} \tau} \delta g_{\alpha}(\mathbf{x}) p^{\mathrm{eq}}(\mathbf{x})\right) . \tag{B8}
\end{align*}
$$

Relation (43) can now be obtained by following the same steps as in the general case, that is, by applying the transformation $\mathbf{x} \rightarrow \boldsymbol{\varepsilon x}$, reversing the magnetic field and interchanging the arguments $\gamma_{w}(t)$ and $\gamma_{q}(t)$ of $L_{\alpha \beta}$, using the symmetry $\delta g_{\alpha}(\mathbf{x})=\delta g_{\alpha}(\boldsymbol{\varepsilon x})$ and performing one integration by parts in the first term.

## APPENDIX C: POSITIVITY OF $\mathbb{A}$

The proof that the matrix $\mathbb{A}$ defined in Eq. (60) is positive semidefinite consists of two major steps. First, for arbitrary numbers $y_{w}, y_{q} \in \mathbb{R}$, we consider the quadratic form

$$
\begin{align*}
\mathcal{Q}_{0}\left(y_{w}, y_{q}\right) & \equiv \sum_{\alpha, \beta=w, q} L_{\alpha \beta} y_{\alpha} y_{\beta}, \\
& =\frac{1}{k_{B}} \int_{0}^{\infty} d \tau\langle\langle G(0) ; G(-\tau)\rangle\rangle \\
& =\frac{1}{k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int_{0}^{\infty} d \tau\left\langle G(t) e^{\tilde{L}^{0 \dagger} \tau} G(t-\tau)\right\rangle \tag{C1}
\end{align*}
$$

where we used the expression (40) for the kinetic coefficients, defined

$$
\begin{equation*}
G(\mathbf{x}, t) \equiv \sum_{\alpha=w, q} y_{\alpha} \delta \dot{g}_{\alpha}(\mathbf{x}, t) \tag{C2}
\end{equation*}
$$

and applied the detailed balance relation (32) to obtain the second line. We recall the definitions (25) for the meaning of the angular brackets. The crucial ingredient for this first step consists of the identity

$$
\begin{align*}
& -\frac{1}{2 k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t\left\langle\int_{0}^{\infty} d \tau e^{\tilde{L}^{0 \dagger} \tau} G(t-\tau)\left(\mathrm{L}^{0 \dagger}+\tilde{\mathrm{L}}^{0 \dagger}\right)\right. \\
& \left.\times \int_{0}^{\infty} d \tau^{\prime} e^{\tilde{L}^{0 \dagger} \tau^{\prime}} G\left(t-\tau^{\prime}\right)\right\rangle  \tag{C3}\\
& =-\frac{1}{2 k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int_{0}^{\infty} d \tau \int_{0}^{\infty} d \tau^{\prime} \\
& \times\left\{\left\langle\left(\left(\partial_{\tau} e^{\tilde{L}^{0 \dagger} \tau} \tau\right) G(t-\tau)\right) e^{\tilde{L}^{0 \dagger} \tau^{\prime}} G\left(t-\tau^{\prime}\right)\right\rangle\right. \\
& \left.+\left\langle\left(e^{\tilde{L}^{0 \dagger} \tau} G(t-\tau)\right)\left(\partial_{\tau^{\prime}} e^{\tilde{L}^{\circ \dagger} \tau^{\prime}}\right) G\left(t-\tau^{\prime}\right)\right\rangle\right\}  \tag{C4}\\
& =\frac{1}{2 k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int_{0}^{\infty} d \tau\left\{2\left\langle G(t) e^{\tilde{L}^{\circ \dagger} \tau} G(t-\tau)\right\rangle\right. \\
& \left.+\partial_{t} \int_{0}^{\infty} d \tau^{\prime}\left\langle\left(e^{\tilde{L}^{0^{\dagger}} \tau} G(t-\tau)\right) e^{\tilde{\mathrm{L}}^{\circ \dagger}} \tau^{\prime} G\left(t-\tau^{\prime}\right)\right\rangle\right\}  \tag{C5}\\
& =\frac{1}{k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t \int_{0}^{\infty} d \tau\left\langle G(t) e^{\tilde{L}^{0 \dagger} \tau} G(t-\tau)\right\rangle \\
& =\mathcal{Q}_{0}\left(y_{w}, y_{q}\right) \text {. } \tag{C6}
\end{align*}
$$

Here, we used the relation

$$
\begin{equation*}
\left\langle A \mathrm{~L}^{0 \dagger} B\right\rangle=\left\langle B \tilde{L}^{0 \dagger} A\right\rangle \tag{C7}
\end{equation*}
$$

which holds for any functions $A(\mathbf{x}), B(\mathbf{x})$ by virtue of the detailed balance condition (32), to obtain Eq. (C4) from Eq. (C3). Expression (C5) follows by applying an integration by parts with respect to $\tau$ and $\tau^{\prime}$, respectively, in the first and the second summand of Eq. (C4). Finally, the second contribution in Eq. (C5) vanishes after carrying out the $t$ integration since the function $G(\mathbf{x}, t)$ is $\mathcal{T}$ periodic in time.

Next, we note that Eq. (32) implies

$$
\begin{align*}
& \left\langle A\left(\mathrm{~L}^{0 \dagger}+\tilde{\mathrm{L}}^{0 \dagger}\right) A\right\rangle \\
& \quad=\int d^{n} \mathbf{x} A(\mathbf{x})\left[\mathrm{L}^{0} p^{\mathrm{eq}}(\mathbf{x})+p^{\mathrm{eq}}(\mathbf{x}) \mathrm{L}^{0 \dagger}\right] A(\mathbf{x}) \\
& \quad=\int d^{n} \mathbf{x}\left[p^{\mathrm{eq}}(\mathbf{x})\right]^{\frac{1}{2}} A(\mathbf{x})\left(\mathrm{K}^{0}+\mathrm{K}^{0 \dagger}\right)\left[p^{\mathrm{eq}}(\mathbf{x})\right]^{\frac{1}{2}} A(\mathbf{x}), \tag{C8}
\end{align*}
$$

where

$$
\begin{equation*}
\mathrm{K}^{0} \equiv\left[p^{\mathrm{eq}}(\mathbf{x})\right]^{-\frac{1}{2}} \mathrm{~L}^{0}\left[p^{\mathrm{eq}}(\mathbf{x})\right]^{\frac{1}{2}} \tag{C9}
\end{equation*}
$$

Since the Hermitian part of this operator is negative semidefinite [41], it follows that Eq. (C8) is nonpositive for any $A(\mathbf{x})$. Hence, we can conclude that the quadratic form $\mathcal{Q}_{0}\left(y_{w}, y_{q}\right)$ is positive semidefinite since it can be written in the form (C3).

For the second step of the proof, we introduce the quadratic form

$$
\begin{equation*}
\mathcal{Q}\left(y_{w}, y_{q}, z\right) \equiv \mathcal{Q}_{0}\left(y_{w}, y_{q}\right)+\mathcal{Q}_{1}\left(y_{w}, y_{q}, z\right) \tag{C10}
\end{equation*}
$$

with

$$
\begin{align*}
& \mathcal{Q}_{1}\left(y_{w}, y_{q}, z\right) \\
& \equiv N_{q q} z^{2}+2 z \sum_{\alpha=w, q} L_{q \alpha} y_{\alpha} \\
& =-\frac{1}{k_{B}}\left(\left\langle\left\langle F \mathrm{~L}^{0 \dagger} F\right\rangle\right\rangle-2\langle\langle F G\rangle\rangle-2 \int_{0}^{\infty} d \tau\langle\langle\dot{F}(0) ; G(-\tau)\rangle\rangle\right) \\
& =-\frac{1}{2 k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t\left\{2\left\langle F(t) \mathrm{L}^{0 \dagger} F(t)\right\rangle-4\langle F(t) G(t)\rangle\right. \\
& \quad-4 \int_{0}^{\infty} d \tau\left\langle\dot{F}(t) e^{\tilde{L}^{\circ} \dagger} \tau\right.  \tag{C11}\\
& \\
& \quad
\end{align*}
$$

where $y_{w}, y_{q}, z \in \mathbb{R}$ and

$$
\begin{equation*}
F(\mathbf{x}, t) \equiv z \delta g_{q}(\mathbf{x}, t) \tag{C12}
\end{equation*}
$$

Note that, in Eq. (C11), we used Eqs. (40) and (61) as well as the detailed balance condition (32). The expression (C11) can be rewritten as

$$
\begin{align*}
& \mathcal{Q}_{1}\left(y_{w}, y_{q}, z\right) \\
&=-\frac{1}{2 k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t\left\{\left\langle F(t)\left(\mathrm{L}^{0 \dagger}+\tilde{\mathrm{L}}^{0 \dagger}\right) F(t)\right\rangle\right. \\
&+\int_{0}^{\infty} d \tau\left\langle F(t)\left(\mathrm{L}^{0 \dagger}+\tilde{\mathrm{L}}^{0 \dagger}\right)\left(e^{\tilde{L}^{0 \dagger} \tau} G(t-\tau)\right)\right\rangle \\
&\left.\left.+\int_{0}^{\infty} d \tau\left\langle e^{\tilde{\mathrm{L}}^{0 \dagger} \tau} G(t-\tau)\right)\left(\mathrm{L}^{0 \dagger}+\tilde{\mathrm{L}}^{0 \dagger}\right) F(t)\right\rangle\right\} . \tag{C13}
\end{align*}
$$

This assertion can be proven by expanding Eq. (C13), invoking Eq. (C7) as well as the identity

$$
\begin{align*}
\mathrm{L}^{0 \dagger} F(\mathbf{x}, t) & =z \mathrm{~L}^{0 \dagger} g_{q}(\mathbf{x}, t)=-z \gamma_{q}(t) \mathrm{L}^{0 \dagger} H_{0}(\mathbf{x}) \\
& =-z \gamma_{q}(t) \tilde{\mathrm{L}}^{0 \dagger} H_{0}(\mathbf{x})=\tilde{\mathrm{L}}^{0 \dagger} F(\mathbf{x}, t) \tag{C14}
\end{align*}
$$

which is implied by condition (36), and integrating by parts, first with respect to $\tau$ and then with respect to $t$, respectively, in the second and the third term showing up in Eq. (C13). Finally, putting together Eqs. (C3) and (C13) leads to

$$
\begin{align*}
& \mathcal{Q}\left(y_{w}, y_{q}, z\right) \\
& =-\frac{1}{2 k_{B} \mathcal{T}} \int_{0}^{\mathcal{T}} d t\left\langle\left(F(t)+\int_{0}^{\infty} d \tau e^{\tilde{L}^{0^{\dagger}} \tau} G(t-\tau)\right)\right. \\
& \left.\quad \times\left(\mathrm{L}^{0 \dagger}+\tilde{\mathrm{L}}^{0 \dagger}\right)\left(F(t)+\int_{0}^{\infty} d \tau^{\prime} e^{\tilde{L}^{0 \dagger}} \tau^{\prime} G\left(t-\tau^{\prime}\right)\right)\right\rangle . \tag{C15}
\end{align*}
$$

The average showing up in this expression is of the form (C8) and thus must be nonpositive. Consequently, we have $\mathcal{Q}\left(y_{w}, y_{q}, z\right) \geq 0$ for any $y_{w}, y_{q}, z$. Moreover, since

$$
\begin{equation*}
\mathcal{Q}\left(y_{w}, y_{q}, z\right)=\mathbf{y}^{t} \mathbb{A} \mathbf{y} \tag{C16}
\end{equation*}
$$

with $\mathbf{y} \equiv\left(z, y_{w}, y_{q}\right)^{t}$, it follows that the matrix $\mathbb{A}$ must be positive semidefinite and thus the proof is completed.

## APPENDIX D: OPTIMAL PROTOCOL

The aim is to determine the optimal protocol $\gamma_{w}^{*}(t)$, which maximizes the rescaled output power
$\bar{P} \equiv \frac{P}{T_{\mathrm{c}} \mathcal{F}_{q}^{2}}=-\left(L_{w w} \chi^{2}+L_{w q} \chi\right) \quad$ with $\quad \chi \equiv \mathcal{F}_{w} / \mathcal{F}_{q}$
for a given time dependence of the bath temperature $g_{q}(t)$ and normalized efficiency

$$
\begin{equation*}
\bar{\eta}=-\frac{L_{w w} \chi^{2}+L_{w q} \chi}{L_{q w} \chi+L_{q q}} \tag{D2}
\end{equation*}
$$

This task is captured by the objective functional

$$
\begin{align*}
\mathcal{P}\left[\gamma_{w}(t), \gamma_{q}(t), \lambda\right] \equiv & (\lambda-1) \chi^{2} L_{w w}+(\lambda-1) \chi L_{w q} \\
& +\lambda \bar{\eta} \chi L_{q w}+\lambda \bar{\eta} L_{q q} \tag{D3}
\end{align*}
$$

where the additional constraint (D2) is taken into account by introducing the Lagrange multiplier $\lambda$. By inserting Eq. (72), Eq. (D3) becomes

$$
\begin{align*}
\mathcal{P}\left[\gamma_{w}(t), \gamma_{q}(t), \lambda\right]= & \frac{1}{\mathcal{T}} \int_{0}^{\mathcal{T}} d t \sum_{\alpha, \beta=w, q} u_{\alpha \beta}\left\{\dot{\gamma}_{\alpha}(t) \gamma_{\beta}(t)\right. \\
& \left.-\int_{0}^{\infty} d \tau \dot{\gamma}_{\alpha}(t) \dot{\gamma}_{\beta}(t-\tau) e^{-2 \mu \kappa_{0} \tau}\right\} \tag{D4}
\end{align*}
$$

Here, we introduced the coefficients

$$
\left(\begin{array}{cc}
u_{w w} & u_{w q}  \tag{D5}\\
u_{q w} & u_{q q}
\end{array}\right) \equiv-2 k_{B} T_{\mathrm{c}}^{2}\left(\begin{array}{cc}
(\lambda-1) \chi^{2} \xi_{w}^{2} & (\lambda-1) \chi \xi_{w} \xi_{q} \\
\lambda \bar{\eta} \chi \xi_{w} \xi_{q} & \lambda \bar{\eta} \xi_{q}^{2}
\end{array}\right)
$$

for notational simplicity. The convolution-type structure of Eq. (D4) naturally suggests solving the variational problem by a Fourier transformation. We expand

$$
\begin{equation*}
\gamma_{\alpha}(t) \equiv \sum_{n \in \mathbb{Z}} c_{n}^{\alpha} e^{i n \omega t} \quad \text { with } \quad \omega \equiv 2 \pi / \mathcal{T} \tag{D6}
\end{equation*}
$$

and thus obtain

$$
\begin{align*}
& \mathcal{P}\left[\gamma_{w}(t), \gamma_{q}(t), \lambda\right] \\
& \quad=\left(-2 \mu \kappa_{0}\right) \sum_{\alpha, \beta=w, q} \sum_{n \in \mathbb{Z}} u_{\alpha \beta} c_{n}^{\alpha} c_{-n}^{\beta} \frac{i n \omega}{i n \omega-2 \mu \kappa_{0}} . \tag{D7}
\end{align*}
$$

Since Eq. (D7) is quadratic in the Fourier coefficients $c_{n}^{\alpha}$, it is straightforward to carry out the optimization with respect to $c_{n}^{w}$. Taking into account that the protocols must be real and therefore $c_{-n}^{\alpha}=c_{n}^{\alpha *}$, the conditions

$$
\begin{align*}
& \partial_{c_{n}^{w}} \mathcal{P}\left[\gamma_{w}(t) \gamma_{q}(t), \lambda\right] \stackrel{!}{=} 0,  \tag{D8}\\
& \partial_{c_{n}^{w *}} \mathcal{P}\left[\gamma_{w}(t), \gamma_{q}(t), \lambda\right] \stackrel{!}{=} 0 \tag{D9}
\end{align*}
$$

yield

$$
\begin{equation*}
c_{n}^{w}=-\left(\frac{u_{w q}+u_{q w}}{2 u_{w w}}+2 i \mu \kappa_{0} \frac{u_{w q}-u_{q w}}{2 n \omega u_{w w}}\right) c_{n}^{q} \tag{D10}
\end{equation*}
$$

for $n \neq 0$. Note that Eq. (D7) does not depend on $c_{0}^{\alpha}$, and thus the optimal protocol will be unique only up to a trivial offset $c_{0}^{w}$. To comply with the constraint (D2), the Lagrange multiplier $\lambda$ must be chosen such that

$$
\begin{equation*}
\partial_{\lambda} \mathcal{P}\left[\gamma_{w}(t), \gamma_{q}(t), \lambda\right]=0, \tag{D11}
\end{equation*}
$$

where the derivative has to be taken before the $c_{n}^{w}$ are replaced by the solution (D10). After some algebra, Eq. (D11) reduces to the simple condition

$$
\begin{equation*}
\bar{\eta}^{2}-(\lambda-1)^{2}(\bar{\eta}-1)^{2}=0 \tag{D12}
\end{equation*}
$$

which is fulfilled for

$$
\begin{equation*}
\lambda_{ \pm}=(1-\bar{\eta} \pm \bar{\eta}) /(1-\bar{\eta}) \tag{D13}
\end{equation*}
$$

Inserting Eqs. (D13) and (D10) into Eq. (D7) yields

$$
\begin{equation*}
\bar{P}_{+} \equiv \mathcal{P}\left[\gamma_{w}(t), \gamma_{q}(t), \lambda_{+}\right]=0 \tag{D14}
\end{equation*}
$$

$$
\begin{align*}
\bar{P}_{-} & \equiv \mathcal{P}\left[\gamma_{w}(t), \gamma_{q}(t), \lambda_{-}\right]=8 k_{B} T_{\mathrm{c}}^{2} \mu \kappa_{0} \xi_{q}^{2} \bar{\eta}(1-\bar{\eta}) \sum_{n=1}^{\infty}\left|c_{n}^{q}\right|^{2} \\
& =\frac{k_{B} T_{\mathrm{c}}^{2} \mu \kappa_{0}}{\mathcal{T}} \bar{\eta}(1-\bar{\eta}) \int_{0}^{\mathcal{T}} d t\left(\gamma_{q}(t)-\bar{\gamma}_{q}\right)^{2}, \quad \text { (D15) } \tag{D15}
\end{align*}
$$

where $\bar{\gamma}_{q}$ is defined in Eq. (75). Consequently, the relevant solution for the Lagrange multiplier is given by $\lambda_{-}$. Finally, the optimal protocol $\gamma^{*}(t, \eta)$ is obtained by summing up the Fourier series (D6). The explicit result (74) can be found by first evaluating

$$
\begin{align*}
\dot{\gamma}_{w}^{*}(t, \eta) & =i \omega \sum_{n \in \mathbb{Z}} n c_{n}^{w} e^{i n \omega t} \\
& =-\sum_{\substack{n \in \mathbb{Z} \\
n \neq 0}}\left(\frac{i n \omega\left(u_{w q}+u_{q w}\right)}{2 u_{w w}}-2 \mu \kappa_{0} \frac{u_{w q}-u_{q w}}{2 u_{w w}}\right) c_{n}^{q} e^{i n \omega t} \\
& =-\frac{u_{w q}+u_{q w}}{2 u_{w w}} \dot{\gamma}_{q}(t)+2 \mu \kappa_{0} \frac{u_{w q}-u_{q w}}{2 u_{w w}}\left[\gamma_{q}(t)-\bar{\gamma}_{q}\right] \\
& =-\frac{2 k_{B} T_{\mathrm{c}}}{\chi}\left(2 \mu \kappa_{0}(1-\bar{\eta})\left[\gamma_{q}(t)-\bar{\gamma}_{q}\right]-\bar{\eta} \dot{\gamma}_{q}(t)\right) \tag{D16}
\end{align*}
$$

and, second, by solving the simple differential equation (D16).
[1] P. G. Steeneken, K. Le Phan, M. J. Goossens, G. E. J. Koops, G. J. A. M. Brom, C. van der Avoort, and J. T. M. van Beek, Piezoresistive Heat Engine and Refrigerator, Nat. Phys. 7, 354 (2011).
[2] V. Blickle and C. Bechinger, Realization of a MicrometerSized Stochastic Heat Engine, Nat. Phys. 8, 143 (2011).
[3] M. Ribezzi-Crivellari and F. Ritort, Free-Energy Inference from Partial Work Measurements in Small Systems, Proc. Natl. Acad. Sci. U.S.A. 111, E3386 (2014).
[4] J. V. Koski, V.F. Maisi, J. P. Pekola, and D. V. Averin, Experimental Realization of a Szilard Engine with a Single Electron, Proc. Natl. Acad. Sci. U.S.A. 111, 13786 (2014).
[5] J. P. Pekola, Towards Quantum Thermodynamics in Electronic Circuits, Nat. Phys. 11, 118 (2015).
[6] I. A. Martínez, É. Roldán, L. Dinis, D. Petrov, and R. A. Rica, Adiabatic Processes Realized with a Trapped Brownian Particle, Phys. Rev. Lett. 114, 120601 (2015).
[7] H. B. Callen, Thermodynamics and an Introduction to Thermostatics, 2nd ed. (John Wiley \& Sons, New York, 1985).
[8] Y. Izumida and K. Okuda, Onsager Coefficients of a FiniteTime Carnot Cycle, Phys. Rev. E 80, 021121 (2009).
[9] Y. Izumida and K. Okuda, Onsager Coefficients of a Brownian Carnot Cycle, Eur. Phys. J. B 77, 499 (2010).
[10] Y. Izumida and K. Okuda, Linear irreversible heat engines based on the local equilibrium assumptions, arXiv:1501.03987v4.
[11] P. Jung, Periodically Driven Stochastic Systems, Phys. Rep. 234, 175 (1993).
[12] L. Onsager, Reciprocal Relations in Irreversible Processes I, Phys. Rev. 37, 405 (1931).
[13] L. Onsager, Reciprocal Relations in Irreversible Processes II, Phys. Rev. 38, 2265 (1931).
[14] T. Schmiedl and U. Seifert, Efficiency at Maximum Power: An Analytically Solvable Model for Stochastic Heat Engines, Europhys. Lett. 81, 20003 (2008).
[15] M. Esposito, R. Kawai, K. Lindenberg, and C. Van den Broeck, Quantum-Dot Carnot Engine at Maximum Power, Phys. Rev. E 81, 041106 (2010).
[16] S. Abe, Maximum-Power Quantum-Mechanical Carnot Engine, Phys. Rev. E 83, 041117 (2011).
[17] A. E. Allahverdyan, K. V. Hovhannisyan, A. V. Melkikh, and S. G. Gevorkian, Carnot Cycle at Finite Power: Attainability of Maximal Efficiency, Phys. Rev. Lett. 111, 050601 (2013).
[18] V. Holubec, An Exactly Solvable Model of a Stochastic Heat Engine: Optimization of Power, Power Fluctuations and Efficiency, J. Stat. Mech. P05022 (2014).
[19] T. E. Humphrey and H. Linke, Quantum, Cyclic, and Particle-Exchange Heat Engines, Physica (Amsterdam) 29E, 390 (2005).
[20] G. Benenti, G. Casati, T. Prosen, and K. Saito, Colloquium: Fundamental Aspects of Steady State Heat to Work Conversion, arXiv:1311.4430v1.
[21] T. E. Humphrey, R. Newbury, R. P. Taylor, and H. Linke, Reversible Quantum Brownian Heat Engines for Electrons, Phys. Rev. Lett. 89, 116801 (2002).
[22] T. E. Humphrey and H. Linke, Reversible Thermoelectric Nanomaterials, Phys. Rev. Lett. 94, 096601 (2005).
[23] R. S. Whitney, Most Efficient Quantum Thermoelectric at Finite Power Output, Phys. Rev. Lett. 112, 130601 (2014).
[24] R. S. Whitney, Finding the Quantum Thermoelectric with Maximal Efficiency and Minimal Entropy Production at Given Power Output, Phys. Rev. B 91, 115425 (2015).
[25] M. Esposito, K. Lindenberg, and C. Van den Broeck, Thermoelectric Efficiency at Maximum Power in a Quantum Dot, Europhys. Lett. 85, 60010 (2009).
[26] B. Sothmann, R. Sánchez, and A. N. Jordan, Thermoelectric Energy Harvesting with Quantum Dots, Nanotechnology 26, 032001 (2015).
[27] F. L. Curzon and B. Ahlborn, Efficiency of a Carnot Engine at Maximum Power Output, Am. J. Phys. 43, 22 (1975).
[28] C. Van den Broeck, Thermodynamic Efficiency at Maximum Power, Phys. Rev. Lett. 95, 190602 (2005).
[29] M. Esposito, K. Lindenberg, and C. Van den Broeck, Universality of Efficiency at Maximum Power, Phys. Rev. Lett. 102, 130602 (2009).
[30] U. Seifert, Stochastic Thermodynamics, Fluctuation Theorems and Molecular Machines, Rep. Prog. Phys. 75, 126001 (2012).
[31] G. Benenti, K. Saito, and G. Casati, Thermodynamic Bounds on Efficiency for Systems with Broken TimeReversal Symmetry, Phys. Rev. Lett. 106, 230602 (2011).
[32] K. Saito, G. Benenti, G. Casati, and T. Prosen, Thermopower with Broken Time-Reversal Symmetry, Phys. Rev. B 84, 201306(R) (2011).
[33] D. Sánchez and L. Serra, Thermoelectric Transport of Mesoscopic Conductors Coupled to Voltage and Thermal Probes, Phys. Rev. B 84, 201307(R) (2011).
[34] M. Horvat, T. Prosen, G. Benenti, and G. Casati, Railway Switch Transport Model, Phys. Rev. E 86, 052102 (2012).
[35] K. Brandner, K. Saito, and U. Seifert, Strong Bounds on Onsager Coefficients and Efficiency for Three-Terminal Thermoelectric Transport in a Magnetic Field, Phys. Rev. Lett. 110, 070603 (2013).
[36] K. Brandner and U. Seifert, Multi-terminal Thermoelectric Transport in a Magnetic Field: Bounds on Onsager Coefficients and Efficiency, New J. Phys. 15, 105003 (2013).
[37] V. Balachandran, G. Benenti, and G. Casati, Efficiency of Three-Terminal Thermoelectric Transport under Broken Time-Reversal Symmetry, Phys. Rev. B 87, 165419 (2013).
[38] J. Stark, K. Brandner, K. Saito, and U. Seifert, Classical Nernst Engine, Phys. Rev. Lett. 112, 140601 (2014).
[39] K. Brandner and U. Seifert, Bound on Thermoelectric Power in a Magnetic Field within Linear Response, Phys. Rev. E 91, 012121 (2015).
[40] B. Sabass, Network Topology with Broken Onsager Symmetry Allows Directional and Highly Efficient Energy Transfer, Europhys. Lett. 110, 20002 (2015).
[41] H. Risken, The Fokker-Planck Equation, 2nd ed. (Springer, New York, 1996).
[42] It is well known that Eq. (29) leads to a unique, periodic distribution $p^{\mathrm{c}}(\mathbf{x}, t)$ in the long time limit if the diffusion matrix is strictly positive definite [11,43]. However, it is readily seen that this assertion still holds for physically meaningful scenarios with a singular diffusion matrix such as the underdamped dynamics described by Kramer's equation [41].
[43] J. Owedyk and A. Kociszewski, On the Fokker-Planck Equation with Time-Dependent Drift and Diffusion Coefficients and Its Exponential Solution, Z. Phys. B 59, 69 (1985).
[44] R. Kubo, M. Toda, and N. Hashitsume, Statistical Physics IINonequilibrium Statistical Mechanics, 2nd ed. (Springer Series in Solid-State Sciences, Berlin, 1998).
[45] L. Machura, M. Kostur, F. Marchesoni, P. Talkner, P. Hänggi, and J. Luczka, Optimal Strategy for Controlling Transport in Inertial Brownian Motors, J. Phys. Condens. Matter 17, S3741 (2005).
[46] U. Seifert, Efficiency of Autonomous Soft Nanomachines at Maximum Power, Phys. Rev. Lett. 106, 020601 (2011).
[47] C. Van den Broeck, N. Kumar, and K. Lindenberg, Efficiency of Isothermal Molecular Machines at Maximum Power, Phys. Rev. Lett. 108, 210602 (2012).
[48] The function (59) diverges as $x$ approaches -1 from below. The following argument, however, shows that this singularity is only apparent. In order to obtain Eq. (55), we have fixed $\eta$ by setting

$$
\mathcal{F}_{w}=-\mathcal{F}_{q} \frac{L_{q q}}{L_{w q}}\left(\frac{(\bar{\eta}+x) y}{2(1+y)}-\sqrt{\left(\frac{(\bar{\eta}+x) y}{2(1+y)}\right)^{2}-\frac{\bar{\eta} x y}{1+y}}\right) .
$$

For $y=h(x), \quad x<-1$ and $\eta=\eta_{\mathrm{C}}$, this expression reduces to

$$
\mathcal{F}_{w}=\mathcal{F}_{q} \frac{L_{q q}}{L_{w q}} \frac{2 x}{x+1} .
$$

Consequently, because of the linear response assumption $\left|\mathcal{F}_{w}\right| \ll \bar{E} / T_{\mathrm{c}}$, Eq. (59) is only valid for

$$
\mathcal{F}_{q} L_{q q} \ll \frac{\bar{E}}{T_{\mathrm{c}}}\left|L_{w q}\right| \frac{x+1}{2 x},
$$

where $\bar{E}$ denotes the typical energy scale of the unperturbed system.
[49] D. Abreu and U. Seifert, Extracting Work from a Single Heat Bath through Feedback, Europhys. Lett. 94, 10001 (2011).
[50] M. Bauer, D. Abreu, and U. Seifert, Efficiency of a Brownian Information Machine, J. Phys. A: Math. Theor. 45, 162001 (2012).
[51] Z. C. Tu, Stochastic Heat Engine with the Consideration of Inertial Effects and Shortcuts to Adiabaticity, Phys. Rev. E 89, 052148 (2014).
[52] F. Berger, T. Schmiedl, and U. Seifert, Optimal Potentials for Temperature Ratchets, Phys. Rev. E 79, 031118 (2009).
[53] Here, we have chosen the constant $\gamma_{0}$ showing up in Eq. (73) as

$$
\begin{equation*}
\gamma_{0}=-\frac{\kappa_{0} \eta_{\mathrm{C}}}{2 \kappa}\left(\bar{\eta}-\frac{\mu \kappa_{0} \mathcal{T}(1-\bar{\eta})}{\pi} \sqrt{1+d} \cdot \operatorname{arccot}[\sqrt{d}]\right) \tag{D17}
\end{equation*}
$$

such that

$$
\int_{0}^{\mathcal{T}} d t \gamma_{w}^{*}(t, \eta, d)=0
$$

ensuring that the constant part of the potential is included in $H_{0}(\mathbf{x})$.
[54] T. Schmiedl and U. Seifert, Optimal Finite-Time Processes in Stochastic Thermodynamics, Phys. Rev. Lett. 98, 108301 (2007).
[55] O. Abah, J. Roßnagel, G. Jacob, S. Deffner, F. SchmidtKaler, K. Singer, and E. Lutz, Single-Ion Heat Engine at Maximum Power, Phys. Rev. Lett. 109, 203006 (2012).
[56] S. An, J.-N. Zhang, M. Um, D. Lv, Y. Lu, J. Zhang, Z.-Q. Yin, H. T. Quan, and K. Kim, Experimental Test of the Quantum Jarzynski Equality with a Trapped-Ion System, Nat. Phys. 11, 193 (2015).


[^0]:    Published by the American Physical Society under the terms of the Creative Commons Attribution 3.0 License. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

