Thermodynamic bounds and general properties of optimal efficiency and power in linear responses

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We study the optimal exergy efficiency and power for thermodynamic systems with Onsager-type “current-force” relationship describing the linear-response to external influences. We derive, in simple analytic forms, the maximum efficiency and optimal efficiency for maximum power for a thermodynamic machine described by a $N \times N$ symmetric Onsager matrix with arbitrary $N$. The figure of merit is expressed in terms of the largest eigenvalue of the “coupling matrix” which is solely determined by the Onsager matrix. Some simple but general relationships between the power and efficiency at the conditions for (i) maximum efficiency and (ii) optimal efficiency for maximum power are obtained. We show how the second law of thermodynamics bounds the optimal efficiency and the Onsager matrix, and relate those bounds together. The maximum power theorem (Jacobi’s Law) is generalized to all thermodynamic machines in the linear-response regime. We also discuss systems with asymmetric Onsager matrix (such as systems under magnetic field) where the reversible limit of efficiency can be reached at finite output power. Cooperative effects are found to improve the figure of merit significantly in systems with multiply cross-correlated responses. Application to example systems demonstrates that the theory is helpful in guiding the search for high performance materials and structures in energy researches.

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I. INTRODUCTION

Under challenges imposed by increasing demand yet limited availability of energy resources, improving energy efficiency becomes increasingly important in technology developments. Historically, Carnot deduced that for a heat engine operating between two reservoirs with temperatures $T_h$ and $T_c$ ($T_h > T_c$), the energy conversion efficiency, $\eta = W/Q$ ($W$ is the output work, $Q$ is the heat from the hot reservoir), has a maximum value, namely the Carnot efficiency, $\eta_C = (T_h - T_c)/T_h$. The Carnot efficiency is only for ideal machines operating in the reversible limit. Energy efficiency of realistic machines is reduced by unavoidable irreversible entropy production. A way to count the reduction of energy efficiency from the value at reversible limit is to use the exergy efficiency (or “second-law efficiency”)[2–7]

$$\phi \equiv \frac{\dot{A}_{\text{out}}}{\dot{A}_{\text{in}}}$$

where $\dot{A}_{\text{out}}$ and $\dot{A}_{\text{in}}$ are the output and input exergy (i.e., the Gibbs free energy) per unit time. Exergy is defined as $A = U - TS$ where $U$ is the enthalpy (i.e., the total energy), $T$ is the temperature, and $S$ is the entropy. Although the total energy is conserved, the output exergy is reduced by entropy production, $\dot{S}_{\text{tot}}$, as $\dot{A}_{\text{out}} = \dot{A}_{\text{in}} - T\dot{S}_{\text{tot}}$, hence $\phi \leq 1$. Both $\phi \leq 1$ and $\eta \leq \eta_C$ are dictated by the second law of thermodynamics. In fact for thermoelectric engine and refrigerator the two are related by[2, 5, 6, 8]

$$\phi = \frac{\eta}{\eta_C}. \quad (2)$$

For this reason, exergy efficiency is also called as “ratio- nal efficiency”[2]. Using Onsager’s theory of irreversible thermodynamics and the exergy efficiency, the study of efficiency of heat engines, chemical engines, and other energy devices can be presented in an uniform manner[2–8]. Specifically, the efficiency of chemical engines, the output work divided by the chemical work, is precisely Eq. (1), as the output work is equal to the output exergy and the input chemical work is equal to the input (consumed) exergy[2–8]. The exergy efficiency becomes particularly convenient for machines with multiple forms of input (or output) energy[7]. For example in a spin- thermoelectric[9] refrigerator, both electrical energy and magnetic energy are consumed to drive the cooling (see Sec. VI B).

A central issue in energy application is to find out the optimal efficiency and maximum power of a machine and the conditions that realize them[10–12]. For example, Ioffe derived the optimal exergy efficiency for isotropic thermoelectric materials in the linear-response regime[13]

$$\eta_{max} = \eta_C \frac{Z}{\sqrt{Z + 1} + \frac{1}{2}}, \quad Z = \frac{\sigma^2 T}{\kappa}. \quad (3)$$

The figure of merit, $Z$, is solely determined by the transport coefficients of the material: the electrical conductivity $\sigma$, the Seebeck coefficient $S$, and the thermal conductivity $\kappa$. This property is an important guiding principle in the search for high performance thermoelectric materials[4–10].

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II. BASIC FORMALISM

Under external influences (“forces”) a thermodynamic system develops motions that deviate from their equilibrium values. These motions (“currents”) can be described quantitatively by the rates of changes in thermodynamic state variables. The relation between the forces $\mathbf{F}$ and currents $\mathbf{j}$ is generally written as

$$\mathbf{j} = \mathbf{M} \mathbf{F} \quad \text{or} \quad J_n = \sum_k M_{nk} F_k. \quad (4)$$

where the index $n \ (k)$ numerates all currents (forces), and $\mathbf{M}$ is the Onsager matrix. When the forces are not too strong the dependence of $\mathbf{M}$ on the forces can be ignored. Cross-correlated responses (e.g., thermoelectric effect) allow energy conversion from the input forms to the output forms and realize functions of a machine. According to
the theory of irreversible thermodynamics\cite{22, 26}, there are an equal number of forces and currents. Each force \( F_n \) has a conjugated current \( J_n \) such that the reduction of total exergy (Gibbs free energy) is given by

\[
- \dot{A}_{\text{tot}} = T \dot{S}_{\text{tot}} = \sum_n J_n F_n.
\]  

(5)

The reduction of exergy \(- \dot{A}_n = J_n F_n \) associated with the current \( J_n \) for exergy input is positive, while for exergy output it is negative. Hence the input and output exergy are

\[
\dot{A}_{\text{in}} = \sum_{n \in I} J_n F_n, \quad \dot{A}_{\text{out}} = - \sum_{k \in O} J_k F_k,
\]

(6)

respectively. The sets \( I \) and \( O \) in the above refer to exergy input and output, respectively. The output exergy is also the output work, i.e., \( \dot{W} = \dot{A}_{\text{out}} \) (Throughout this paper “work” is associated with linear-response processes for given thermodynamic forces, i.e., work and efficiency are functions of thermodynamic forces). For \( \dot{A}_{\text{in}} > 0 \) the exergy efficiency is

\[
\phi = \frac{- \sum_{k \in O} J_k F_k}{\sum_{n \in I} J_n F_n} = \frac{\dot{A}_{\text{in}} - T \dot{S}_{\text{tot}}}{\dot{A}_{\text{in}}} \leq 100\%.
\]

(7)

Only in the reversible limit, \( \dot{S}_{\text{tot}} = 0 \), the exergy efficiency \( \phi \) reaches its upper bound. The second law of thermodynamics requires \( \dot{S}_{\text{tot}} \geq 0 \) for all possible values of forces. This is satisfied only when all eigenvalues of the Onsager matrix \( M \) are positive \cite{see Appendix A} (note that, as the reversible limit, \( \dot{S}_{\text{tot}} = 0 \), does not exist for realistic systems, we consider only situations with positive entropy production. Zero entropy production is the limit when the entropy production is extremely small. In this way, all eigenvalues of the Onsager matrix must be greater than zero.) This property is briefly stated as that \textit{Onsager matrix is positive.}

### III. Optimizing Efficiency and Power for Systems with Symmetric Onsager Matrix

The maximum exergy efficiency is obtained by solving the differential equation

\[
\partial_{\vec{F}_i} \phi = 0, \quad \forall k.
\]

(8)

Previous attempts of solving the above equations\cite{6, 17, 22} have ended up with very complicated calculations and discussions. This is because for a \( N \times N \) Onsager matrix, there are \( N(N + 1)/2 \) independent response coefficients (if the Onsager matrix is symmetric). Besides, there are \( N - 1 \) coupled differential equations to solve (from Eqs. (4) and (7), scaling all forces by a constant does not change \( \phi \); this property reduces the number of differential equations to be solved by one). Solving these equations analytically becomes a formidable task when \( N \geq 3 \) (see, e.g., the rather complicated discussions in Ref. \cite{7}). In this work we manage to solve the problem analytically in a particularly simple way.

We notice that the force-current relation can be rewritten as

\[
\begin{pmatrix}
\vec{J}_O \\
\vec{J}_I
\end{pmatrix} =
\begin{pmatrix}
\hat{M}_{OO} & \hat{M}_{OI} \\
\hat{M}_{IO} & \hat{M}_{II}
\end{pmatrix}
\begin{pmatrix}
\vec{F}_O \\
\vec{F}_I
\end{pmatrix},
\]

(9)

where the symbols \( O \) and \( I \) are used to abbreviate the indices of forces and currents for exergy output and input, respectively. E.g., \( \vec{J}_O \) is the vector of the output current and \( \hat{M}_{OO} \) is the matrix relating the output force vector \( \vec{F}_O \) to the output current vector \( \vec{J}_O \). For symmetric Onsager matrix (i.e., time-reversal symmetric systems), \( \hat{M}_{II} = \hat{M}_{II}^T, \hat{M}_{IO} = \hat{M}_{IO}^T, \) and \( \hat{M}_{OO} = \hat{M}_{OO}^T \) where the superscript \( T \) stands for matrix (vector) transpose.

From Eqs. (7), (8), and (9), we find that

\[
\partial_{\vec{F}_O} \dot{A}_{\text{out}} = \phi_{\text{max}} (\partial_{\vec{F}_O} \dot{A}_{\text{in}})
\]

(10)

which gives

\[
\vec{F}_O = - \frac{1 + \phi_{\text{max}}}{2} \hat{M}_{OO}^{-1} \hat{M}_{OI} \vec{F}_I.
\]

(11)

The inverse of the matrix \( \hat{M}_{OO} \) is justified as \( \hat{M}_{OO} \) is a positive matrix. Inserting this into Eq. (10) we obtain

\[
\phi_{\text{max}} = \frac{\frac{1}{2} (1 - \phi_{\text{max}}^2)}{1 - \frac{1 + \phi_{\text{max}}}{\lambda}}
\]

(12)

where \( \lambda \equiv \max(\hat{A}), \langle \hat{A} \rangle \equiv \langle \vec{g}^T \hat{\Lambda} \vec{g} \rangle, \vec{g} \) is a normalized vector (i.e., \( \vec{g}^T \vec{g} = 1 \)) defined as

\[
\vec{g} \equiv \hat{M}_{II}^{-1/2} \vec{F}_I / \sqrt{\vec{F}_I^T \hat{M}_{II} \vec{F}_I},
\]

(13)

and

\[
\hat{\Lambda} \equiv \hat{M}_{II}^{-1/2} \hat{M}_{IO} \hat{M}_{OO}^{-1} \hat{M}_{OI} \hat{M}_{II}^{-1/2}.
\]

(14)

The inverse square root of the matrix \( \hat{M}_{II} \) is well-defined since \( \hat{M}_{II} \) is a positive matrix \cite{see Appendix A}.

Eq. (12) is now a quadratic equation that can be solved analytically. The physical solution with \( \phi_{\text{max}} < 1 \) is

\[
\phi_{\text{max}} = \frac{\sqrt{Z + 1} - 1}{\sqrt{Z + 1} + 1}, \quad Z = \frac{\lambda}{1 - \lambda}
\]

(15)

where \( Z \) is the figure of merit and \( \lambda \) is called the “degree of coupling”\cite{6, 12}. We call the matrix \( \hat{\Lambda} \) as the “coupling matrix.” Finally, \( \vec{F}_I \) or the normalized vector \( \vec{g} \) must be tuned to maximize \( \langle \hat{A} \rangle \). The maximum value is achieved when \( \vec{g} \) equals to the eigenvector of \( \hat{\Lambda} \) which corresponds to the largest eigenvalue. This gives

\[
\lambda = \text{largest eigenvalue of } \hat{\Lambda}.
\]

(16)
It is proven in Appendix B that $\lambda \leq 1$ as bounded by the second law of thermodynamics. The $\lambda \to 1$ limit can be reached only in the reversible limit when the determinant of the Onsager matrix is zero $^{29}$.

Eq. (19) presents one of the main result in this work. This result has not been found in Ref. [3], despite rather complicated treatment there. Previously the coupling matrix was also introduced for the discussion of piezoelectric energy conversion in Ref. $^{29}$. We extend the concept to general thermodynamic systems in this work.

The output power $W = A_{\text{out}}$ at maximum exergy efficiency is

$$\hat{W}(\phi_{\text{max}}) = \frac{1}{4}(1 - \phi_{\text{max}}^{2})\lambda \left(\vec{\hat{F}}_{I}^{T} \hat{M}_{II} \vec{\hat{F}}_{I}\right). \quad (17)$$

We now study the exergy efficiency for maximum power. The physical concern is to optimize the output power by tuning the output forces $\vec{\hat{F}}_{O}$ which corresponds to adjusting the response of the device accepting the output energy to maximize the output power (as will be shown in the next section). The output power is then optimized at $\partial_{\vec{\hat{F}}_{O}} A_{\text{out}} = 0$ which renders $\vec{\hat{F}}_{O} = -\frac{1}{2} \hat{M}_{OO}^{-1} \hat{M}_{OI} \vec{\hat{F}}_{I}$. The equation for $\phi$ can be established by inserting the above into Eq. (11) which is then solved in a way similar to the solution of Eq. (12). After that we optimize $\phi$ by tuning the input forces $\vec{\hat{F}}_{I}$ and then obtain the optimal exergy efficiency for maximum power

$$\phi_{\text{opt}}(W_{\text{max}}) = \frac{Z}{2(Z + 2)} \leq 50\%, \quad (18)$$

where $Z$ is given in Eq. (14) and $\lambda$ is again the largest eigenvalue of the coupling matrix $\Lambda$. The above expression is consistent with the well-known result that the upper limit of the exergy efficiency for maximum power for systems with symmetric Onsager matrix is $50\%$. $^{2,8,30}$ The above derivations also provide a solid proof of the upper bound, 50%, for general thermodynamic systems in the linear-response regime. The maximum output power is found to be

$$W_{\text{max}} = \frac{1}{4} \lambda \left(\vec{\hat{F}}_{I}^{T} \hat{M}_{II} \vec{\hat{F}}_{I}\right). \quad (19)$$

Comparing the exergy efficiencies and output powers for the two optimization schemes discussed in this section, we find that

$$\frac{\phi_{\text{opt}}(W_{\text{max}})}{\phi_{\text{max}}} = \frac{1}{1 + \phi_{\text{max}}^{2}}, \quad \frac{\hat{W}(\phi_{\text{max}})}{W_{\text{max}}} = 1 - \phi_{\text{max}}^{2}. \quad (20)$$

Remarkably, the above two simple relationships hold for all thermodynamic machines with symmetric Onsager matrix in the linear-response regime (thermodynamic systems with asymmetric Onsager matrix is discussed in Sec. V). The above two relationships bear very important information on the optimal efficiencies and powers which is one of the main contributions in this work. Fig. III represents them graphically. Particularly in the reversible limit $\phi_{\text{max}} = 1$, the output power at maximum efficiency vanishes $^{31}$ and the efficiency at maximum power reaches 50%. At low efficiency limit, $\phi_{\text{max}} \ll 100\%$, the power and efficiency at the two optimal conditions are almost the same. Considerable differences between the two optimal conditions appear only when $\phi_{\text{max}} \gtrsim 10\%$ or $Z \gtrsim 1$ ($\lambda \gtrsim 0.5$).

We remark that the largest eigenvalue of $\hat{M}_{II}^{-1/2} \hat{M}_{IO} \hat{M}_{OO}^{-1} \hat{M}_{OI} \hat{M}_{II}^{1/2}$ is the same as the largest eigenvalue of $\hat{M}_{OO}^{-1/2} \hat{M}_{OI} \hat{M}_{II}^{1/2} \hat{M}_{IO} \hat{M}_{OO}^{-1/2}$ (proof is given in Appendix B). Particularly in thermoelectric energy conversion, this means that the figures of merit for the engine, refrigerator, and heat pump are the same. Another way to express the results in Eqs. (15) and (16) is

$$Z + 1 = \text{Large eigenvalue of } \hat{M}_{II}^{1/2}(\hat{M}^{-1})_{II} \hat{M}_{II}^{1/2},$$

or

$$Z + 1 = \text{Large eigenvalue of } \hat{M}_{OO}^{1/2}(\hat{M}^{-1})_{OO} \hat{M}_{OO}^{1/2},$$

where $\hat{M}^{-1}$ is the inverse of the Onsager matrix $\hat{M}$. Particularly when there is only one force $F_{k}$ for exergy input (or output), the figure of merit is given by

$$Z = \frac{M_{kk} m_{kk}}{\text{Det}(\hat{M})} - 1, \quad (21)$$

where $m_{kk}$ and Det($\hat{M}$) are the $(kk)$ minor and the determinant of the Onsager matrix $\hat{M}$, respectively. These properties can be used to simplify the calculation of the figure of merit when one of the two is easier to calculate.
positive matrices. As a consequence the degree of cou-

FIG. 2. (Color online) Schematic of realistic thermodynamic 

IV. REALISTIC CONSIDERATIONS: OUTPUT 

The currents for energy input into the operating system 

M_{oi} \tilde{J}_I.

\[ \tilde{F}_O = -(\tilde{M}_{oo} + \tilde{M}_L)^{-1} \tilde{M}_{oi} \tilde{F}_I. \]

The power consumed by the device is

\[ \tilde{F}_O^T \tilde{M}_L \tilde{F}_O = \tilde{F}_I^T \tilde{M}_{10} (\tilde{M}_{oo} + \tilde{M}_L)^{-1} \tilde{M}_L \times (\tilde{M}_{oo} + \tilde{M}_L)^{-1} \tilde{M}_{oi} \tilde{F}_I. \]

The input exergy is

\[ \tilde{F}_I \tilde{J}_I = \tilde{F}_I^T (\tilde{M}_{11} - \tilde{M}_{10} (\tilde{M}_{oo} + \tilde{M}_L)^{-1} \tilde{M}_{oi}) \tilde{F}_I. \]

The exergy efficiency is then

\[ \phi = \frac{\tilde{F}_I \tilde{M}_L \tilde{F}_O}{\tilde{F}_I \tilde{J}_I}. \]

We find that the maximum output power is reached at

\[ \tilde{M}_L = \tilde{M}_{oo}. \]

whereas the maximum exergy efficiency is reached when

\[ \tilde{M}_L = \sqrt{1 - \lambda \tilde{M}_{oo}}. \]

At these conditions we obtain again Eqs. (15), (17), (18), 

and (19). The above results reflect the importance of 

matching between the response of the device \( \tilde{M}_L \) and 

that of the system \( \tilde{M}_{oo} \) in optimizing the efficiency and 

output power \( \tilde{W} \). Particularly, Eq. (28) generalizes the 

maximum power theorem (Jacobi’s Law) to all thermo-

dynamic machines in the linear-response regime.

There are two possible schemes of adjusting the input 

forces, \( \tilde{F}_I \), to optimize the performance of the machine. 

The first scheme is to optimize the efficiency, i.e., to optimize \( \lambda \). This has been discussed in Sec. III. This scheme 

reflects balance between optimizing output power and 

efficiency which is relevant to some biological and ecolo-

gical systems \( \tilde{W} \). The second scheme is to adjust \( \tilde{F}_I \) 

for further optimization of the output power. This will 

lead to efficiency smaller or equal to that in Eq. (15). 

Hence the exergy efficiency for this scheme is also not 

larger than 50%. From Eqs. (13) and (19) one finds that

\[ W_{max} = \frac{1}{\lambda} \tilde{F}_I^T \tilde{M}_{10} \tilde{M}_{oo}^{-1} \tilde{M}_{oi} \tilde{F}_I. \]

The above can be optimized to be

\[ W_{max} = \frac{1}{\lambda \Upsilon} \left( \tilde{F}_I^T \tilde{F}_I \right), \]

with \( \Upsilon \) being the largest eigenvalue of the matrix \( \tilde{M}_{10} \tilde{M}_{oo}^{-1} \tilde{M}_{oi} \). It can be 

shown that \( \Upsilon \) is positive [see Appendix B]. There is no 

obvious upper bound on it that is imposed by the laws 

of logical systems \([2]\). The second scheme is to adjust

\[ \tilde{W} = \frac{1}{\lambda} \tilde{F}_I^T \tilde{M}_{10} \tilde{M}_{oo}^{-1} \tilde{M}_{oi} \tilde{F}_I. \]

the parasitic dissipation. The effect is described by the following phe-

nomenological equations

\[ \tilde{J}_p = \tilde{M}_{pp} \tilde{F}_p, \quad \tilde{J}_o = \tilde{M}_{oo} \tilde{F}_o. \]

Here the superscript \( p \) stands for parasitic dissipation. The 

currents for energy input into the operating system becomes \( \tilde{J}_I + \tilde{J}_p \). And the currents that load into the 

device becomes \( \tilde{J}_O + \tilde{J}_o \). The equivalent circuit is de-

picted in Fig. 2. Taking into account of those parasitic 

currents modifies the response coefficients as

\[ \tilde{M}_{11} \rightarrow \tilde{M}_{11} + \tilde{M}_{pp}, \quad \tilde{M}_{oo} \rightarrow \tilde{M}_{oo} + \tilde{M}_{po}. \]

Parasitic dissipation increases the eigenvalues of the matrices \( \tilde{M}_{11} \) and \( \tilde{M}_{oo} \) because both \( \tilde{M}_{pp} \) and \( \tilde{M}_{po} \) are positive matrices. As a consequence the degree of coupling \( \lambda \) and the figure of merit \( Z \) are reduced, according to Eqs. (13) and (15). This is consistent with the physical picture that part of the useful energy is consumed by the parasitic dissipation.

Energy from the operating system can be outputted to 

(i) a huge reservoir (e.g., a power grid with huge capac-

ity), or to (ii) a finite device. The optimization presented 

in Sec. III is for option (i) where the output current \( \tilde{J}_o \) 

does not induce any observable effect on the huge reser-

voir which in turn modifies the force \( \tilde{F}_o \), so that \( \tilde{J}_o \) and 

\( \tilde{F}_o \) are uncorrelated. In electrical circuit analog, it is 

equivalent to using the output energy to charge a huge 

capacitor where the charging current \( \tilde{J}_o \) does not change 

the voltage across the capacitor \( \tilde{F}_o \). For option (ii) if the 

response of the device is \( \tilde{J}_o = \tilde{M}_1 \tilde{F}_o \), the Kirchoff’s 

current law requires that \( \tilde{J}_o + \tilde{J}_p = 0 \). Therefore,

\[ \tilde{F}_o = -(\tilde{M}_{oo} + \tilde{M}_L)^{-1} \tilde{M}_{oi} \tilde{F}_I. \]
of thermodynamics (except maybe in the zero temperature limit [33]). The above derivation is meaningful only when all input thermodynamic forces \( F_n \) (\( \forall n \in I \)) are measured in the same physical unit and scale. This requirement is usually not satisfied for systems with more than one type of input forces (e.g., if both mechanical and electrical forces are used for energy input). Discussion on this scheme of performance optimization depends on specific systems which is of little interest for our purpose.

V. OPTIMAL EXERGY EFFICIENCY AND POWER FOR SYSTEMS WITH ASYMMETRIC ONSAGER MATRIX

We now study systems with asymmetric Onsager matrix. We first note that \( \hat{F}_I^T \hat{M}_{II} \hat{F}_I = \hat{F}_I^T \hat{M}_{II} \hat{F}_I \) and \( \hat{F}_O^T \hat{M}_{OO} \hat{F}_O = \hat{F}_O^T \hat{M}_{OO} \hat{F}_O \) where \( \hat{M}_{II} = \frac{1}{2} \left( \hat{M}_{II} + \hat{M}_{II}^T \right) \) and \( \hat{M}_{OO} = \frac{1}{2} \left( \hat{M}_{OO} + \hat{M}_{OO}^T \right) \). This property is due to the symmetry of the summation over indices of forces.

It is hard to derive the optimal exergy efficiency and power for general systems with asymmetric Onsager matrix. Here we focus on a special situation where \( \hat{M}_{OI} = r \hat{M}_{II} \hat{M}_{IO} \) with \( r \) being a real number. For this particular situation, from Eq. (10), we find \( \hat{F}_O = -\frac{1}{1+r^{-1} \phi_{max}} \hat{M}_{OO}^{-1} \hat{M}_{OI} \hat{F}_I \). Inserting this into Eq. (1) and solving the equation for \( \phi_{max} \), we obtain

\[
\phi_{max} = r \frac{\sqrt{Z+1} - 1}{\sqrt{Z+1} + 1}
\]

(30)

where \( Z \) is given by the same expression as in Eqs. (15) and (16) but with \( \hat{M}_{II} \) and \( \hat{M}_{II}^T \) replaced by their symmetric counterparts \( \hat{M}_{II}^O \) and \( \hat{M}_{II}^T \). The exergy efficiency for maximum power is given by

\[
\phi_{opt}(\hat{W}_{max}) = \frac{r Z}{2(Z+2)}
\]

(31)

From the second law of thermodynamics the restriction on \( \lambda \) is [see Appendix B]

\[
\frac{4r}{(1+r)^2} \leq \lambda < 0, \text{ if } r < 0, \quad \frac{4r}{(1+r)^2} \leq 0 \leq \frac{4r}{(1+r)^2}, \text{ if } r \geq 0.
\]

(32a, 32b)

The above restrictions give rise to \( Z + 1 = \frac{1}{1-\lambda} \geq 0 \) and \( r(\sqrt{Z+1} - 1) > 0 \), so that the optimal exergy efficiency given in Eq. (30) is positive and well-defined.

The maximum possible, i.e., the upper bound of exergy efficiency is reached at \( \lambda = \frac{4r}{(1+r)^2} \) as

\[
\phi_{bound} = r^2, \text{ if } |r| < 1, \quad \phi_{bound} = 1, \text{ if } |r| \geq 1.
\]

(33a, 33b)

The dissipation at the upper bound exergy efficiency is

\[
T \hat{S}_{tot} = (1-r)^2 \left( \hat{F}_I^T \hat{M}_{II} \hat{F}_I \right), \quad \text{if } |r| < 1, \quad T \hat{S}_{tot} = 0, \quad \text{if } |r| \geq 1.
\]

(34a, 34b)

The entropy production for \( |r| < 1 \) is always positive hence the upper bound efficiency is not 100%.

The upper bound of the exergy efficiency for maximum power is also reached at \( \lambda = \frac{4r}{(1+r)^2} \) with

\[
\phi_{opt}(\hat{W}_{max})|_{bound} = \frac{r^2}{r^2 + 1}.
\]

(35)

From the above equation the Curzon-Ahlfors limit of exergy efficiency [8, 11] \( \phi_{CA} = 50\% \) can be overcome when \( |r| > 1 \). This is first pointed out by Benenti et al. in the study of thermoelectric efficiency in systems with broken time-reversal symmetry [19].

The output power at maximum exergy efficiency is

\[
\hat{W}(\phi_{max}) = \frac{1}{4}(1-r^{-2} \phi_{max}^2) r \lambda \left( \hat{F}_I^T \hat{M}_{II} \hat{F}_I \right).
\]

(36)

Combining the above with Eq. (33), the upper bound of efficiency for \( |r| < 1 \) is \( \phi = r^2 \) so that the output power is positive. For \( |r| > 1 \) the maximum efficiency can reach 100% without conflicting the requirement of positive output power. The maximum output power is

\[
\hat{W}_{max} = \frac{1}{4} r \lambda \left( \hat{F}_I^T \hat{M}_{II} \hat{F}_I \right).
\]

(37)

We find that

\[
\frac{\phi_{max}}{\phi_{opt}(\hat{W}_{max})} = 1 + r^{-2} \phi_{max}^2, \quad \frac{\hat{W}(\phi_{max})}{\hat{W}_{max}} = 1 - r^{-2} \phi_{max}^2.
\]

(38a, 38b)

Eqs. (33b) and (38b) reveal that for systems with asymmetric Onsager matrix with \( |r| > 1 \), the output power is nonzero even when \( \phi_{max} \) reaches the value of 100% in the reversible limit. These results agree with the findings of Benenti et al. on thermoelectric efficiency and power in time-reversal symmetry broken systems [19].

It is interesting to study the optimal exergy efficiency and power of the reversed machine (i.e., the machine with output input reversed). The output power of the reversed machine is \( -\hat{F}_O^T \hat{F}_I = -\hat{A}_{in} \), while the input power becomes \( \hat{F}_O^T \hat{J}_O = -\hat{A}_{out} \). The reversed machine is working in the region with \( \hat{A}_l < 0 \). The efficiency of the reversed machine is defined as

\[
\phi' = \frac{\hat{A}_{in}}{\hat{A}_{out}}.
\]

(39)

We find that the optimal exergy efficiency and powers are similar but with \( r \) replaced by \( r^{-1} \). Therefore for \( |r| > 1 \) the reversed machine cannot reach the efficiency
The output power is \( \dot{W} = \frac{2x-1-r^2}{x^2-r^2} \) (41)

For all values of \( r \) the reversible limit \( T\dot{S}_{tot} = 0 \) is reached at \( x = 1 \). When \( r = 1, 100\% \) efficiency is reached by both the machine and the reversed machine at \( x = 1 \) where the input and output output as well as entropy production vanish [see Fig. 3]. For \( |r| < 1 \), the machine cannot reach 100\% efficiency, but the reversed machine can reach 100\% efficiency with finite output power, because at \( x = 1 \) the machine is operating in the reversed mode [see Fig. 3]. For \( |r| > 1 \), the output power of the machine is positive at \( x = 1 \), thus the machine can reach 100\% efficiency with finite output power [see Fig. 3].

In systems with broken time-reversal symmetry, such as two-dimensional electron systems under perpendicular magnetic field, Hall effect, and Nernst-Ettingshausen effect give rise to asymmetric Onsager matrix \([34, 35]\). The asymmetric Onsager matrix can be decomposed into the symmetric part and anti-symmetric part. Specifically,

\[
\hat{\mathcal{M}}_{1O} = \hat{\mathcal{M}}_{1O}^s + \hat{\mathcal{M}}_{1O}^a, \quad \hat{\mathcal{M}}_{OI} = \hat{\mathcal{M}}_{OI}^s + \hat{\mathcal{M}}_{OI}^a
\]  

(42)

with \( \hat{\mathcal{M}}_{1O}^s = (\hat{\mathcal{M}}_{1O}^a)^T \) and \( \hat{\mathcal{M}}_{1O}^a = - (\hat{\mathcal{M}}_{1O}^s)^T \). The symmetric part, \( \hat{\mathcal{M}}_{1O}^s \), is related to entropy production and is restricted by the second law of thermodynamics. The anti-symmetric part, \( \hat{\mathcal{M}}_{1O}^a \), however, does not contribute to dissipation and is often related to Berry phase effects [55].

The output and input exergy can be written as

\[
\dot{A}_{out} = \dot{A}_{out}^s - \hat{\mathcal{F}}_{O}^{T} \hat{\mathcal{M}}_{OI}^s \hat{\mathcal{F}}_{I}, \quad \dot{A}_{in} = \dot{A}_{in}^s - \hat{\mathcal{F}}_{O}^{T} \hat{\mathcal{M}}_{OI}^a \hat{\mathcal{F}}_{I}
\]  

(43)

where \( \dot{A}_{out}^s \) and \( \dot{A}_{in}^s \) are the output and input exergy for the symmetrized Onsager matrix with

\[
\dot{A}_{out}^s = - \hat{\mathcal{F}}_{O}^{T} \hat{\mathcal{M}}_{OI}^s \hat{\mathcal{F}}_{I} - \hat{\mathcal{F}}_{I}^{T} \hat{\mathcal{M}}_{OI}^s \hat{\mathcal{F}}_{O}, \quad \dot{A}_{in}^s = \hat{\mathcal{F}}_{I}^{T} \hat{\mathcal{M}}_{IO}^s \hat{\mathcal{F}}_{O} + \hat{\mathcal{F}}_{O}^{T} \hat{\mathcal{M}}_{IO}^s \hat{\mathcal{F}}_{I}.
\]

The additional term in Eq. (43), \( \hat{\mathcal{F}}_{O}^{T} \hat{\mathcal{M}}_{OI}^a \hat{\mathcal{F}}_{I} \), does not cause entropy production, but shift the input and output powers by the same magnitude. In this way the reversible limit is shifted from the boundary between the machine and the reversed machine, into the operating region of the machine or the reversed machine, whichever has positive output power in such limit.

VI. APPLICATION TO REALISTIC SYSTEMS

A. Example I: Thermoelectric energy conversion in isotropic systems

Thermoelectric transport equation for an isotropic system is given by

\[
\left( \begin{array}{c} \dot{j} \\ \dot{j}_q \\ \end{array} \right) = \left( \begin{array}{cc} \sigma & \sigma ST \\ \sigma ST & \kappa T + \sigma S^2 T^2 \end{array} \right) \left( \begin{array}{c} \dot{\xi} \\ \dot{\nabla} T/T \end{array} \right),
\]

(44)
where the electric field \( \vec{E} \) include both the external and induced electric fields. Here \( \sigma \) is the electrical conductivity, \( S \) is the Seebeck coefficient, and \( \kappa \) the thermal conductivity. The efficiency, or coefficient of performance, of a thermoelectric refrigerator is

\[
\eta \equiv \frac{\dot{Q}}{W} = \frac{T}{\Delta T} \frac{\vec{j}_q \cdot \nabla T / T}{\vec{E}} = \eta_C \phi, \quad \eta_C \equiv \frac{T}{\Delta T}. \tag{45}
\]

For a slab of thickness \( \ell_z \) with temperature gradient and electric field along the direction \( z \) which is perpendicular to the slab plane, the temperature difference is \( \Delta T = -\ell_z \frac{dT}{dz} > 0 \) for \( \frac{dT}{dz} < 0 \). The maximum coefficient of performance \( \eta_{\text{max}} \) is related to the maximum exergy efficiency by

\[
\eta_{\text{max}} = \eta_C \phi_{\text{max}} = \eta_C \frac{\sqrt{Z + 1} - 1}{\sqrt{Z + 1}}. \tag{46}
\]

where the figure of merit is

\[
Z = \frac{\sigma S^2 T}{\kappa}. \tag{47}
\]

This recovers the well-known thermoelectric figure of merit as found by Ioffe.

B. Example II: Spin-thermoelectric effect

In conducting magnetic materials charge, spin, and thermal transports are coupled together. There coupleings are called spin-thermoelectric or spin-caloric effect. In isotropic materials spin-thermoelectric effect is described by the following transport equation:

\[
\begin{align*}
\left( \begin{array}{c}
\frac{\vec{j}_s}{\vec{j}_q} \\
\frac{\vec{j}_s}{\vec{j}_q}
\end{array} \right) &= \left( \begin{array}{cc}
\frac{\sigma P}{\sigma P} & \frac{\sigma ST}{P \sigma ST} \\
\frac{\sigma ST}{P \sigma ST} & \kappa_0 T
\end{array} \right) \left( \begin{array}{c}
\vec{E} \\
-\nabla m
\end{array} \right). \tag{48}
\end{align*}
\]

where \( \vec{j}_s = \vec{j}_s^{(s)} + \vec{j}_s^{(d)} \), \( \vec{j}_q = \vec{j}_q^{(s)} - \vec{j}_q^{(d)} \) with \( \vec{j}_s^{(s)} \) and \( \vec{j}_q^{(d)} \) denoting the electrical currents of the spin-up and spin-down electrons, respectively. \( \vec{E} = -\nabla \mu / e \) with \( \mu \equiv (\mu_\uparrow + \mu_\downarrow) / 2 \), and \( m \equiv (\mu_\uparrow - \mu_\downarrow) / (2e) \) where \( \mu_\uparrow \) and \( \mu_\downarrow \) are the electrochemical potentials for spin-up and spin-down electrons, respectively, \( e \) is the carrier charge. \( \sigma \) is the electrical conductivity, \( S \) is the Seebeck coefficient, \( P \) and \( P' \) are two dimensionless quantities describing spin polarization of carriers, \( \kappa_0 \) is the heat conductivity at \( \vec{E} = \nabla m = 0 \). Microscopically they are given by

\[
\begin{align*}
\sigma &= \int dE \left( \frac{-\partial n_F}{\partial E} \right) \sum_s \sigma^{(s)}(E), \tag{49a}
\end{align*}
\]

\[
\begin{align*}
P &= \langle s_z \rangle, \quad S = \langle E \rangle / eT, \tag{49b}
\end{align*}
\]

\[
\begin{align*}
P' &= \langle E s_z \rangle / \langle E \rangle, \quad \kappa_0 T = e^{-2} \sigma \langle E^2 \rangle. \tag{49c}
\end{align*}
\]

with \( \sigma^{(s)}(E) (s = \uparrow, \downarrow) \) being spin- and energy-dependent conductivity. We have set the energy zero to be at the (equilibrium) chemical potential, i.e., \( \mu \equiv 0 \). \( s_z = 1 \) or \( -1 \) for spin up and down, respectively. \( n_F = 1 / \left[ \exp(\frac{E}{\kappa_0 T}) + 1 \right] \) is the Fermi distribution of the carrier. The averages in the above equations are defined as

\[
\langle O \rangle = \sigma^{-1} \int dE \left( -\frac{\partial n_F}{\partial E} \right) \sum_s \sigma^{(s)}(E)O. \tag{50}
\]

The above equations can be viewed as Mott relations [37] generalized to spin-dependent transport. It assumes elastic transport (by which the energy dependent conductivity is well-defined) and fails when inelastic transport processes become important as pointed out by the author and collaborators [38].

We consider refrigeration driven by both the electric field \( \vec{E} \) and the spin density gradient \( \nabla m \). The coefficient of performance of the refrigerator is defined as

\[
\eta \equiv \frac{\dot{Q}}{W} = \frac{T}{\Delta T} \frac{\vec{j}_q \cdot \nabla T / T}{\vec{E}} = \eta_C \phi, \quad \eta_C = \frac{T}{\Delta T}. \tag{51}
\]

Schematic of spin-thermoelectric cooling is shown in Fig. 11. Consider a slab of thickness \( \ell_z \) where the temperature gradient, electric field, and spin density gradient are along the direction perpendicular to the slab plane, i.e., the \( z \) direction. The temperature difference is \( \Delta T = -\ell_z \frac{dT}{dz} > 0 \) for \( \frac{dT}{dz} < 0 \). The maximum coefficient of performance is again related to the maximum exergy efficiency as given in Eq. (46). Using Eqs. (47) and (48) we obtain

\[
Z = \frac{\sigma TS^2 (1 - 2PP' + P^2)}{\kappa_0 (1 - P^2) - \sigma TS^2 (1 - 2PP' + P^2)}. \tag{52}
\]

Remarkably one can show that the above degree of coupling is greater than the figure of merit for thermoelectric cooling,

\[
Z_{\text{TE}} = \frac{\sigma TS^2}{\kappa_0 - \sigma TS^2}, \tag{53}
\]

and the figure of merit for spin-Feltier cooling [39, 40],

\[
Z_{\text{SP}} = \frac{\sigma TS^2 P^2}{\kappa_0 - \sigma TS^2 P^2}. \tag{54}
\]

This interesting phenomenon has a geometric origin which is understood as follows. The electric field and the spin-density gradient can be parametrized as

\[
\vec{E} = \vec{F}_0 \cos \theta, \quad -\nabla m = -\vec{F}_0 \sin \theta \tag{55}
\]

where \( \vec{F}_0 = 6 e \sqrt{\frac{1}{2\pi^2} (|\nabla \mu|_1^2 + |\nabla \mu|_2^2)} \) with \( \vec{F}_0 \) being the transport direction, \( |\vec{F}_0| \) is the total “magnitude” of the input force. The heat current,

\[
\vec{j}_q = \vec{j}_q0 + \vec{j}_q1 + \vec{j}_{q2}, \tag{56}
\]
efficient spin-thermoelectric cooling demands large Seebeck coefficient. According to the literature, large Seebeck coefficient ranging from 100 to 45000 μV/K can be attained in magnetic or strongly-correlated semiconductors and magnetic tunnel junctions. Sizable figure of merit, \( Z \sim 1 \), however, is still to be achieved.

The figure of merit at fixed θ is found as

\[
Z(\theta) = \frac{\sigma S^2 T(P' \sin \theta + \cos \theta)^2 (1 + 2P \sin \theta \cos \theta)}{\kappa_0 - \sigma S^2 T(P' \sin \theta + \cos \theta)^2 (1 + 2P \sin \theta \cos \theta)}
\]

The maximum exergy efficiency is achieved at \( \theta = \theta_M \) with

\[
\tan \theta_M = \frac{P' - P}{1 - P'P}.
\]

C. Example III: Piezoelectric, piezomagnetic and magnetoelectric effects

Piezoelectric energy harvest has been studied extensively and made into useful devices. There is also the piezomagnetic effect where elastic strain induces a magnetization or vice versa. These two effects are common in ferroelectric and ferromagnetic insulators. Materials with simultaneous ferroelectric and ferromagnetic properties, or more generally multiple spontaneous electric and magnetic orders, are called multiferroics. An important technologically property of multiferroics is the magnetoelectric effect which offers efficient conversion between electric and magnetic energy in the
and spin-Peltier cooling as a function of $P'$, the enhancement of figure of merit due to cooperative effect, $Z/\max(Z_{TF}, Z_{SP})$, as a function of $P$ and $P'$. The parameters are $S = 50 \mu V/K$ and $T = 300$ K. The heat conductivity is $\kappa_0 = \sigma L T$ with the Lorenz number of $L = 2.5 \times 10^{-8}$ W Ω K$^{-2}$. The white region in (b) near $P = 1$ is forbidden by the second law of thermodynamics.

Radio frequency regime. Wood and Austin suggested many possible applications of the magnetoelectric effect, among which are as transducers which convert the microwave magnetic field into microwave electric field, attenuators which are used to improve impedance matching in circuits, and ultrasensitive magnetic field sensors. Multiferroics with strong magnetoelectric response have been the aim of extensive studies. Recently, strong magnetoelectric response were found in both crystalline (such as CaMnO$_3$[48], TbMnO$_3$[49], and HoMnO$_3$[50]) and nano-composite (such as BiFeO$_3$ thin film heterostructures[51] and BaTiO$_3$-CoFe$_2$O$_4$ nano-structures[52]) materials. In many of these materials the interplay of piezoelectric and piezomagnetic responses play an important role. In fact, multiferroics can be made from nano-composites of ferroelectric and ferromagnetic compounds where elastic strain at interfaces mediate coupling between electric and magnetic polarizations[46, 53].

In these materials a full description of responses to external mechanical, electric, and magnetic forces are given by

$$\hat{S} \hat{D} = \begin{pmatrix} \hat{s} & \hat{d} & \hat{q} \\ \hat{T} & \hat{E} & \hat{B} \end{pmatrix} \left( \begin{pmatrix} \hat{d}^T & \hat{c} & \hat{a} \\ \hat{q}^T & \alpha^T & \hat{\mu}_m \end{pmatrix} \hat{T} \hat{E} \hat{B} \right). \tag{59}$$

where the forces are stress $\hat{T}$, electric field $\hat{E}$, and magnetic field $\hat{B}$, the currents are strain $\hat{S}$, electric displacement $\hat{D}$, and magnetic induction $\hat{B}$. Here $\hat{D}$ and $\hat{B}$ stand for the values deviate from the equilibrium ones (which could be nonzero in materials with spontaneous polarization and magnetization). The response matrix has the dimension of $12 \times 12$. Specifically, $\hat{s}$ is the $6 \times 6$ compliance tensor, $\hat{c}$ is the $3 \times 3$ dielectric tensor, $\hat{\mu}_m$ is the $(3 \times 3)$ permeability tensor, $\hat{d}$ describes piezoelectric response, $\hat{q}$ describes piezomagnetic response, and $\hat{\alpha}$ gives magnetoelectric response.

In general the response matrix is frequency dependent. Experiments have shown resonance behavior in magnetoelectric response[54]. Without further complication of specific circuits set-up for energy conversion at finite frequencies[55, 56], here we consider the low-frequency limit which is sufficient to demonstrate the underlying principles. Extension of study to finite frequency regimes will be achieved in future works. First, the coupling matrix for piezoelectric energy conversion is

$$\hat{\Lambda}_{pe} = \hat{c}^{-1/2} \hat{d}^T \hat{s}^{-1} \hat{d} \hat{c}^{-1/2}, \tag{60}$$

which coincides with the electromechanical coupling matrix given in Ref. [18]. The largest electromechanical coupling factor of a material is given by the largest eigenvalue of the coupling matrix $\hat{\Lambda}_{pe}$. Piezoelectric effect allows harvest of mechanical energy to power portable and isolated electrical systems as well as small motors which have already found applications[43]. Existing materials have already shown large electromechanical coupling factors, reaching to $\gtrsim 0.5$[55, 56], which allows efficient piezoelectric energy conversion. In realistic systems, additional mechanical and electrical damping reduces the efficiency[55, 56]. Although further complication must be considered for a finite frequency set-up with a mechanical oscillator, the efficiency is still an increasing function of the electromechanical coupling factor[55, 56]. Piezomagnetic effect can be used for magnetic field sensing, stress sensing, and mechanical generation of spinwaves[44]. The coupling matrix for piezomagnetic energy conversion is

$$\hat{\Lambda}_{pm} = \hat{\mu}_m^{-1/2} \hat{q}^T \hat{s}^{-1} \hat{q} \hat{\mu}_m^{-1/2}. \tag{61}$$

The largest piezomagnetic coupling factor is the largest eigenvalue of the above matrix. Piezomagnetic coupling factor can be as large as 0.5 as well[58]. The coupling matrix for magnetoelectric energy conversion is

$$\hat{\Lambda}_{em} = \hat{\mu}_m^{-1/2} \hat{d}^T \hat{c}^{-1} \hat{d} \hat{\mu}_m^{-1/2}. \tag{62}$$

Experiments on laminated composites of rare-earth-iron alloys (Terfenol-D) and lead-zirconate-titanate (PZT) achieved a magnetoelectric coefficient along the stacking direction as high as $\alpha_E = \alpha/\epsilon = 10$ V cm$^{-1}$ Oe$^{-1}$. Along this direction the relative dielectric constant is about 1000[57] and the relative permeability is about 4[53]. According to these parameters, the magnetoelectric coupling factor along the stacking direction is around 0.1. The largest magnetoelectric coupling factor is given by the largest eigenvalue of the matrix $\hat{\Lambda}_{em}$.

The system also allows multiple input or output energy forms. For example, magnetic energy can be generated by simultaneously inputting electric and mechanic energy. This yield the coupling matrix of

$$\hat{\Lambda}_{m-pe} = \hat{\mu}_m^{-1/2} \hat{q}_{pe}^{-1} \hat{h}_{pe}^{-1} \hat{\mu}_m^{-1/2} \tag{63}$$

where

$$\hat{q}_{pe} = \left( \begin{pmatrix} \hat{q} \\ \hat{\alpha} \end{pmatrix} \right), \quad \hat{h}_{pe} = \left( \begin{pmatrix} \hat{d} \\ \hat{\delta} \end{pmatrix} \right). \tag{64}$$
Similar to the results in Sec. VII B, cooperative effect will lead to larger degree of coupling from the above coupling matrix. That is, the exergy efficiency is no less than those of piezomagnetic effect and magnetoelectric effect. Significant improvement of efficiency could be possible by the synergetic effect in systems with cross-correlated piezo-electric-magnetic effect.

D. Example IV: Biological energy conversion

Biological processes are driven by various energies: the internal energy produced by oxidation and external energy from environments. Understanding of bioenergetics is one of the most important and challenging task in biology. Many of the processes can be described by Onsager’s linear-response theory (although many others cannot)[2, 5, 64, 62]. One example is transport across a membrane. The flows of various ions, such as Na+, Ca2+, and H+ as well as other materials, such as phosphorylation, oxygen, and sugars are all driven by their density gradients, chemical reaction and other forces[22]. If, e.g., some of these materials involve in a chemical reaction, flows of those materials will be correlated. Synergetic effects will appear as multiple flows take place in cooperative ways. Biological systems, may also utilize the cross-correlation of those flows to optimize energy efficiency. There have been a lot of studies of bioenergetics using irreversible thermodynamics[2, 5, 64, 62]. However, none of them have reached a simple analytic results as obtained in this work.

To demonstrate the usefulness of the theory, we consider a toy model describes the reaction of

\[ A + B \leftrightarrow C + energy, \quad Q + energy + E \leftrightarrow P \]  

(65)

in a reaction center surrounded by a membrane. We assume the reactions are reversible with the help of enzymes. In the former reaction \( A \) and \( B \) are consumed to produce \( C \) while some energy is generated which is absorbed by \( Q \) and \( E \) to form \( P \) (energy stored in \( P \)). We assume that all energy generated in the former reaction is absorbed by the latter one. To describe such a reaction, we use six flows, \( J_A, J_B, J_Q, \) and \( J_E \) to describe the rate of consumption of \( A, B, Q, \) and \( E, -J_C \) and \( -J_P \) to describe the rate of production of \( C \) and \( P \). The flow and reaction is illustrated in Fig. 7. The reaction is described by Eq. 9 in linear-response regime with

\[ \vec{\mathcal{J}}_i = (J_A, J_B, J_Q, J_E)^T, \quad \vec{\mathcal{F}}_i = (J_C, J_P)^T, \]  

(66a)

\[ \vec{\mathcal{F}}_1 = (F_A, F_B, F_Q, F_E)^T, \quad \vec{\mathcal{F}}_O = (F_C, F_P)^T. \]  

(66b)

The forces can be written as \( \vec{\mathcal{F}}_i = \delta \mu_i + a_i \) where \( \delta \mu_i = \mu^\text{out}_i - \mu^\text{in}_i \) with \( \mu^\text{out}_i \) and \( \mu^\text{in}_i \) being the chemical potential of \( i \) outside and inside the reaction center, respectively, \( a_i \) is the affinity of material \( i \) for the reaction which is the free energy of \( i \) per mole (if \( \mathcal{J}_i \) is measured in unit of mole per second). Biological systems can control those flows and their correlations through chemical reaction processes (e.g., via enzymes) as well as selective and tunable transmission of materials through the membrane. The efficiency of the biological reaction is \( \phi = -\vec{\mathcal{F}}_O^\text{T} \vec{\mathcal{J}}_i/(\vec{\mathcal{F}}_i^\text{T} \vec{\mathcal{J}}_i) \). The optimal efficiency is then given by Eq. 11 where the degree of coupling is given by the largest eigenvalue of the coupling matrix \( \Lambda \) given by Eq. 13. This result is much simpler than that discussed in Ref. 7.

VII. CONCLUSION AND DISCUSSIONS

We examined the important question of “what is the maximum efficiency of a thermodynamic machine when its (linear) responses to external is given?”. This question has been answered in simple limits with two thermodynamic currents. It becomes rather difficult to answer for a thermodynamic machine with arbitrarily complex responses. Efforts on the problem in the literature failed in yielding general, analytic results that are useful for applications and engineering. Pushed by fast developing nanotechnology and material technologies, complex systems with advanced (energy) applications play more and more important roles. It becomes increasingly important to extend the known, simple results on efficiency optimization to those complex systems.

The problem is formulated based Onsager’s linear response theory which holds for general thermodynamic systems with steady state transport in linear-response regime. We derived the optimal efficiency and powers for general thermodynamic machines with arbitrary linear-response coefficients. The results are written in simple and analytic forms. Based on those results we establish two general relationships between the optimal efficiency and powers for two realistic optimization schemes: (i)
maximum efficiency and (ii) optimal efficiency for maximum power. We proved that the upper bound efficiency at maximum output power is 50% for all thermodynamic systems with symmetric Onsager response matrix. The results are confirmed by considering realistic energy systems where the output power is consumed by a device of which the response coefficients can be varied. We proved that the maximum output power is reached when the response matrix of the device, $\hat{M}_L$, is equal to that of the power-supply machine in the output sector, $\hat{M}_{OO}$. This proof generalizes the maximum power theorem (Jacobi’s Law) to all thermodynamic machines with symmetric Onsager response matrix in the linear-response regime. We also extend the studies to systems with asymmetric Onsager response matrix where the efficiency at maximum output power can exceed 50%. Besides, in such systems the second law of thermodynamics does not forbid the reversible limit of efficiency, 100%, to be reached at finite output power. Physical explanations are presented by considering dissipationless responses. We also show that such limit can only be reached either by the machine or by the reversed machine, but not both of them.

Several examples are presented to demonstrate applications of the theory. First for isotropic thermoelectric systems, we recover Ioffe’s well-known results. We then consider refrigeration in spin-thermolectric systems. It is shown that driving cooling by both electrochemical potential and spin density gradients yield maximum efficiency higher than when only one of the two gradients (forces) is applied to the system. Such enhancement of maximum efficiency due to cooperative effects between different forces can be significant in certain parameter regimes. We remark that such cooperative effects prevail in systems with multiple cross-correlated responses and can be used to improve energy efficiency for realistic machines. We also apply the theory to discussions of piezoelectric, piezomagnetic, and magnetoelectric energy conversion and their cooperative effects as well as biological energy conversion. Studies in this work shed light on general properties of optimization in energy applications and are helpful in guiding the search for high performance energy materials and systems.

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**Appendix A: Positiveness of Onsager matrix and definition of inverse square root of matrices**

The second law of thermodynamics requires $\dot{S}_{\text{tot}} \geq 0$ for all possible values of forces. That is

$$T \dot{S} = \sum_{nk} F_n M_{nk} F_k \geq 0, \quad \forall \vec{F},$$

$$= \sum_{nk} F_n M^*_{nk} F_k \geq 0, \quad \forall \vec{F}, \quad (A1)$$

where $M^*_{nk} = \frac{1}{N} (M_{nk} + M_{kn})$. Since $\hat{M}^*$ is a real symmetric matrix with dimension $N \times N$, it has $N$ (real) eigenvectors and eigenvalues. For any vector $\vec{F}$ can be decomposed into the eigenvectors,

$$\vec{F} = \sum_{i=1}^{N} f_i \vec{e}_i,$$

where $\vec{e}_i$ corresponding to the eigenvalue $m_i$, then

$$T \dot{S} = \sum_{i} m_i f_i^2. \quad (A3)$$

The above is positive definite only when $m_i \geq 0$ for all $i$. That is, all eigenvalues of the matrix $M^*$ must be positive (In this work we take the situation with $m_i = 0$ as the limit that is approached from the $m_i > 0$ side, which has never been reached in realistic systems).

When $\hat{M}_{II}$ is a real symmetric matrix there always exist an orthogonal matrix $\hat{\Omega}_I$ such that $\hat{M}_{II} = \hat{\Omega}_I^T \hat{D} \hat{\Omega}_I$ where $\hat{D}$ is a diagonal matrix. According to the second law of thermodynamics all the eigenvalues of matrix $\hat{M}_{II}$ are positive. Therefore all the elements of the diagonal matrix $\hat{D}$ are positive. We can then define the inverse square root of $\hat{M}_{II}$ as

$$\hat{M}_{II}^{-1/2} = \hat{\Omega}_I^T \hat{D}^{-1/2} \hat{\Omega}_I. \quad (A4)$$

The inverse square root of $\hat{M}_{OO}$ is defined similarly,

$$\hat{M}_{OO}^{-1/2} = \hat{\Omega}_O^T \hat{B}^{-1/2} \hat{\Omega}_O \quad (A5)$$

where $\hat{M}_{OO} = \hat{\Omega}_O^T \hat{B} \hat{\Omega}_O$, $\hat{\Omega}_O$ is orthogonal, and $\hat{B}$ is diagonal and positive.

**Appendix B: Prove that $\hat{A}$ is a positive matrix, $\lambda \leq 1$, and others**

To simplify the proof, we perform an orthogonal transformation $\hat{\Omega}_I \otimes \hat{\Omega}_I$ on the forces. To keep the currents conjugated with forces, the same transformation must be exerted on the currents. The transformation diagonalize the matrix $\hat{M}_{II}$ and $\hat{M}_{OO}$. As both of them are positive
matrix we can further perform the following transformation

\[ \mathcal{F}_n \rightarrow \mathcal{F}_n \sqrt{M_{nn}}, \quad \mathcal{J}_n \rightarrow \mathcal{J}_n / \sqrt{M_{nn}}. \]  

(B1)

This leads to

\[ M_{nk} \rightarrow \frac{M_{nk}}{\sqrt{M_{nn}M_{kk}}}. \]  

(B2)

After the above transformation the matrix \( \hat{M}_{II} \) and \( \hat{M}_{OO} \) become identity matrix. Now for the real matrix \( \hat{M}_{II} \) there always exists a decomposition \( \hat{M}_{II} = \hat{\omega}_T \hat{C} \hat{\omega}_O \) where \( \hat{\omega}_I \) and \( \hat{\omega}_O \) are orthogonal matrices and \( \hat{C} \) is a diagonal matrix (but no need to be a square matrix) (see Ref. [63]). Performing the orthogonal transformation \( \hat{\omega}_O \otimes \hat{\omega}_I \) on the forces and currents and using Eq. (B1), we obtain

\[ \hat{\Lambda} = \hat{M}_{II} \hat{M}_{II}^\dagger = \hat{C} \hat{C}^T. \]  

(B3)

Now \( \hat{\Lambda} \) is a diagonal matrix with all diagonal elements greater than or equal to zero. We thus proved that the coupling matrix \( \Lambda \) is a positive matrix. The largest eigenvalue of the coupling matrix \( \hat{\Lambda} \) is also positive, i.e., \( \lambda \geq 0 \). Labeling the diagonal elements of \( \hat{C} \) as \( y_n \) \((n = 1, \ldots, N)\) is integer if the dimension of the matrix \( \hat{C} \) is \( N \times N' \) with, say, \( N \geq N' \), the Onsager matrix now becomes

\[ \mathcal{M} = \begin{pmatrix} 1 & 0 & y_1 & 0 & 0 & \cdots & \cdots & 0 \\ 0 & 1 & 0 & y_N & 0 & \cdots & \cdots & 0 \\ y_1 & 0 & 1 & 0 & 0 & \cdots & \cdots & 0 \\ \vdots & \vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & y_N & 0 & 1 & 0 & \cdots & \cdots & 0 \\ \vdots & \vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & 0 & 0 & \cdots & \cdots & 1 \end{pmatrix}. \]  

(B4)

It follows from Eqs. (B3) and (B1) that

\[ \lambda = \max \{ y_n^2 \}. \]  

(B5)

According to the second law of thermodynamics all eigenvalues of the Onsager matrix are positive, i.e.,

\[ 1 + y_n \geq 0, \quad 1 - y_n \geq 0, \quad \forall n, \]  

(B6)

according to Eq. (B4). Therefore \( 0 \leq \lambda \leq 1 \) and the figure of merit \( Z = \lambda / (1 - \lambda) \) is positive definite.

At this point one can also show that when a machine is operating in a reverse way, i.e., the output channels become input channels and vice versa. The matrix \( \mathcal{M} \) becomes \( \hat{\Lambda} = \hat{C}^T \hat{C} \) which has the same largest eigenvalue as before. In this way we proved that when a machine is operated in a reverse way the degree of coupling \( \lambda \) and the figure of merit does not change.

Finally from Eq. (B2) one can also directly show that \( \hat{M}_{II} \hat{M}_{II}^\dagger \hat{M}_{II} = \hat{C} \hat{C}^T \) is positive matrix (i.e., all its eigenvalues are positive). Therefore the largest eigenvalue of \( \mathcal{M}_{II} \mathcal{M}_{OO}^{-1} \mathcal{M}_{II} \) is positive, i.e., \( \mathcal{Y} > 0 \).

Appendix C: Thermodynamic bounds for systems with asymmetric Onsager matrix

We shall focus on the situation considered in the main text where \( \mathcal{M}_{II} = r \hat{M}_{II}^F \). For this situation one can perform the same transformation as in previous section: symmetric matrices \( \mathcal{M}_{II} \) and \( \mathcal{M}_{OO} \) can be diagonalized by orthogonal transformations; after that performing the transformation (B1) and another orthogonal transformation \( \mathcal{M}_{II} \) and \( \mathcal{M}_{OO} \) become identity matrices and \( \mathcal{M}_{II} \rightarrow \hat{C} \), \( \mathcal{M}_{II} \rightarrow r \hat{C}^T \). The second law of thermodynamics requires that all eigenvalues of \( \mathcal{M}^* \) are greater than or equal to zero. Therefore

\[ 1 - \frac{1}{2} (1 + r) y_n \geq 0, \quad 1 + \frac{1}{2} (1 + r) y_n \geq 0, \quad \forall n. \]  

(C1)

The degree of coupling is given by

\[ \lambda = r \max \{ y_n^2 \}. \]  

(C2)

Therefore

\[ 0 \leq \frac{(1 + r)^2}{4r} \leq 1. \]  

(C3)

The discussions in Sec. V can be generalized to the situation when \( \mathcal{M}_{II} \) is not proportional to \( \mathcal{M}_{II} \) but they can still be diagonalized simultaneously by an orthogonal transformation. The diagonal form of \( \mathcal{M}_{II} \) is \( diag \{ y_n \} \) while that of \( \mathcal{M}_{II} \) is \( diag \{ r_n y_n \} \). The optimal exergy efficiency is given by

\[ \phi_{\text{max}} = \max \left\{ r_n \sqrt{Z_n + 1.5 - 1} \right\}, \]  

(C4)

where

\[ Z_n = \frac{\lambda_n}{1 - \lambda_n}, \quad \lambda_n = r_n y_n^2. \]  

(C5)

And the output power at maximum exergy efficiency is

\[ W(\phi_{\text{max}}) = \frac{1}{4} (1 - r_n^2 - \phi_{\text{max}}^2) r_n \lambda_n \left( \bar{\mathcal{F}}^T \hat{M}_{II} \bar{\mathcal{F}}_I \right) \]  

(C6)

for the \( n \) that maximizes the efficiency. The maximum output power is

\[ W_{\text{max}} = \frac{1}{4} \max \left\{ r_n \lambda_n \right\} \left( \bar{\mathcal{F}}^T \hat{M}_{II} \bar{\mathcal{F}}_I \right). \]  

(C7)

The optimal exergy efficiency for maximum power is given by

\[ \phi_{\text{opt}}(W_{\text{max}}) = \frac{r_n' Z_n'}{2(Z_n' + 2)} \]  

(C8)

for the \( n' \) that maximizes the output power (which may be different from that maximizes the efficiency). As \( n \) can be different from \( n' \), the relationship between the two optimal efficiencies and powers can be more complicated then we discussed in the main text.
[48] R. D. Johnson, L. C. Chapon, D. D. Khalyavin, P. Manuel, P. G. Radaelli, and C. Martin, Phys. Rev. Lett. 108, 067201 (2012).
[49] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature 426, 55 (2003).
[50] T. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature 430, 541 (2004).
[51] J. Wang et al., Science 299, 1719 (2003).
[52] H. Zheng et al., Science 303, 661 (2004).
[53] C. W. Nan, Phys. Rev. B 50, 6082 (1994).
[54] U. Laletsin, N. Padubnaya, G. Srinivasan, and C. P. Devreugd, Appl. Phys. A 78, 33 (2004).
[55] C. D. Richards, M. J. Anderson, D. F. Bahr, and R. F. Richards, J. Micromech. Microeng. 14, 717 (2004).
[56] Y. C. Shu and I. C. Lien, J. Micromech. Microeng. 16, 2429 (2006).
[57] J. Ryu, S. Priya, K. Uchino, and H.-E. Kim, J. Electroceram. 8, 107 (2002).
[58] S. Dong, J.-F. Li, and D. Viehland, J. Mater. Sci. 41, 97 (2006).
[59] G. Liu, C.-W. Nan, N. Cai, and Y. Lin, Int. J. Solids Struct. 41, 4423 (2004).
[60] S. R. Caplan, Curr. Top. Bioenerg. 4, 1 (1997).
[61] G. F. Oster, A. S. Perelson, and A. Katchalsky, Q. Rev. Biophys. 6, 1 (1973).
[62] C. Tanford, Annu. Rev. Biochem. 52, 379 (1983).
[63] G. H. Golub and C. F. Van Loan, Matrix Computations 3rd ed. (Johns Hopkins University Press, Baltimore, MD), p. 70-73 (1990).