Thermodynamic coupling rule for far-from-equilibrium systems

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The energy conversion efficiency of far-from-equilibrium systems is generally limited by irreversible thermodynamic fluxes that make contact with different heat baths. For complex systems, the states of the maximum efficiency and the minimum entropy production are usually not equivalent. Here we show that the proper adjustments of the interaction between the energy and matter currents offer some important criteria for the performance characterizations of thermal agents, regardless of the system types and transition protocols. The universal thermodynamic coupling rule plays a critical role in irreversible processes. A double quantum dot system is applied to demonstrate that the performances of heat engines or refrigerators can be enhanced by suitably adjusting the coupling strength between thermodynamic fluxes.

For open inhomogeneous systems, the thermodynamic process driven by a temperature difference between two heat baths is generally irreversible. At a stationary state, the entropy production rate $\sigma$ is greater than or equal to zero, which is exactly balanced by the entropy flow through the terminals [13]. If $\sigma = 0$, the performance of the engine (refrigerator) reaches its limit and the efficiency [coefficient of performance (COP)] will be equal to the Carnot value [14]. However, since all complex natural processes are irreversible, the minimum entropy production rates have been found inefficient to ensure the maximum efficiency and COP [7, 8].

Pietzonka et al. proved that a universal trade-off among the power, efficiency, and constancy exists in nonequilibrium heat engines [9, 10]. Whitney found that the maximum efficiency of an irreversible device occurs when the system lets all particles go through in a certain transmission window, but none at other energies [11]. Benenti et al. pointed out that the upper bound of the maximum efficiency of a thermoelectric generator is reached when the figure of merit $ZT \to \infty$. This limit corresponds to the tight coupling condition, for which the Onsager matrix becomes singular and therefore the ratio of the heat current to the electric current is independent of the applied thermodynamic forces [12–14]. The strong coupling condition can be obtained for a nonelectromechanical device consisting of a single quantum level [15, 16]. More generally, the dissipative thermodynamic fluxes rely on the temperature and chemical potential gradients [17–20]. It is unlikely to identify two quantities involving proportional relationships. The question arises as to whether there are universal principles relevant to the thermodynamic fluxes and forces that provide ways to the maximum efficiency and COP of far-from-equilibrium systems.

Here, we present a novel criterion for attaining the upper bound for the efficiency (COP) of any heat engine (refrigerator) running between two heat baths. Our main result is that the connection between the energy and matter currents is suitable for the performance characterization of thermal agents regardless of the system types and transition protocols. Tracing from the master equation, we start with the analysis of the entropy and the statistics of energy and matter transfers. Results will show that the most convenient optimization technique is to alter the coupling strength of thermodynamic fluxes.

For a non-degenerate system weakly coupled to different environmental modes, the dynamics of the populations satisfies a rate equation

$$\dot{P}_i = \sum_j \mathcal{L}_{ij} P_j = \sum_j \sum_\nu \mathcal{L}_{ij}^{(\nu)} P_j,$$

where $P_i$ is the probability of finding the system in the eigenstate $|i\rangle$, $\mathcal{L}_{ij}$ describes the transfer rate from state $j$ to state $i$, and $\mathcal{L}_{ij}^{(\nu)}$ is the rate contributed by the coupling with the reservoir $\nu$. All possible decays of $P_i$ are contained within the factor $\sum_j \sum_\nu \mathcal{L}_{ij}^{(\nu)}$. When an open inhomogeneous system obeying Eq. (1) is placed in contact with the hot and cold reservoirs (denoted H and C), the entropy production rate due to irreversible processes reads [Supplementary Eq. (S6)]

$$\sigma = -\beta_H J^{(H)} - \beta_C J^{(C)} = (\beta_C - \beta_H) I_E^{(H)} + (\beta_H \mu_H - \beta_C \mu_C) I_M^{(H)},$$

where $J^{(\nu)} = I_E^{(\nu)} - \mu_\nu I_M^{(\nu)}$ describes the heat current entering the system from reservoir $\nu$, $\beta_\nu$ represents the inverse value of the temperature, and $\mu_\nu$ is the chemical potential. The energy current $I_E^{(\nu)}$ and the matter current $I_M^{(\nu)}$ associated with reservoir $\nu$ are positive variables when flowing into the system. The second formula in Eq. (2) has been expressed in terms of the currents entering the system from the hot reservoir, because both energy and matter currents are conserved within the system, i.e., $I_E^{(H)} + I_E^{(C)} = 0$ and $I_M^{(H)} + I_M^{(C)} = 0$. On the basis of Eq. (2), we are able to determine the universal thermodynamic coupling rule for the systems interacting with two terminals. Consider two reservoirs with the
same temperature but at different electrochemical potentials $\mu_C - \mu_H = eV \geq 0$, where $e$ is the positive elementary charge. The transfer of an electron from C to H increases the entropy of the universe by $\beta eV$ independent of the electron energy. For the general case where $\beta_H < \beta_C$ and $\mu_H < \mu_C$, an irreversible process yields $(\beta_C - \beta_H) I_E^{(H)} + (\beta_H \mu_H - \beta_C \mu_C) I_M^{(H)} \geq 0$ (Section 1 in Supplementary). When electrons spontaneously flow from H to C, the system behaves as a heat engine. Under this condition, $I_M^{(H)} > 0$ and the ratio of the energy and matter currents is bounded by

$$I_E^{(H)}/I_M^{(H)} \geq \Theta,$$

where $\Theta = (\beta_C \mu_C - \beta_H \mu_H) / (\beta_C - \beta_H)$. The efficiency of the thermal engine expresses the fraction of heat that becomes useful work, i.e.,

$$\eta = \frac{J^H + J^C}{J^H} = \frac{\mu_C - \mu_H}{I_E^{(H)}/I_M^{(H)} - \mu_H}, \quad (4)$$

If $I_M^{(H)} < 0$, electrons flow spontaneously from C to H, implying that the ratio $I_E^{(H)}/I_M^{(H)}$ has an upper bound given by

$$I_E^{(H)}/I_M^{(H)} \leq \Theta. \quad (5)$$

At this juncture, the system is capable of removing heat from the lower-temperature reservoir. The COP of the refrigerator is the ratio of the heat removed from C to the input work, i.e.,

$$\phi = \frac{J^C}{J^H + J^C} = \frac{I_E^{(H)}I_M^{(H)} - \mu_C}{\mu_C - \mu_H}. \quad (6)$$

Equations (3-6) reveal that the coupling strength $I_E^{(H)}/I_M^{(H)}$ plays an important role in determining the efficiency and COP of the thermal devices regardless of the system complexity. The interplay between the energy and matter currents characterizes the energy conversion performance of physical and biological systems. $\eta (\phi)$ is a linear decreasing (increasing) function of $I_E^{(H)}/I_M^{(H)}$ at given values of $\mu_C$ and $\mu_H$. The criterion function $\Theta$ simply relies on a set of reservoir parameters. This is the main result of the present work: by suitably adjusting the coupling strength between the energy and matter currents, electrons can be transferred nearly reversibly between two reservoirs with arbitrary temperatures and electrochemical potentials.

For a quantum dot with a single transition frequency embedded between two fermionic junctions, the energy and matter currents exhibit tight coupling properties [15]. Every electronic jump carries the same amount of energy $\varepsilon$, yielding the perfect couple situation $I_E^{(H)} = \varepsilon I_M^{(H)}$. At steady state, the entropy production rate turns into $\sigma = [(\beta_C - \beta_H) \varepsilon + (\beta_H \mu_H - \beta_C \mu_C)] I_M^{(H)}$, which is directly proportional to the matter current. Supposing $\varepsilon = \Theta$, we are able to find $\sigma = 0$ and obtain a reversible nanothermoelectric device with the Carnot efficiency or COP. At this particular transition energy, the temperature and electrochemical driving forces cancel each other out, since the two reservoirs behave as if they were in thermodynamic equilibrium [12]. The probability densities for electrons are equal on both sides of the transport channel. This is, however, not the case for a multilevel system, as the transferred energy depends on a specific type of jumping. In general, the energy and matter currents are not in direct proportion and cannot simultaneously tend to zero, resulting in a positive entropy production rate. Maximum efficiency may not correspond to a minimal entropy production for irreversible processes.

To reveal the potential application of the thermodynamic coupling rule mentioned above, we build a DQD system that is weakly coupled to two separate electronic baths. The DQD (Fig. 1) is modeled by the Hamiltonian

$$H_S = \varepsilon_L d_L^d c_h^c + \varepsilon_R d_R^d c_R^c + \varepsilon_R d_R^d c_R^c + T (d_L^d d_R^d + d_R^d d_L^d) + U d_L^d d_L^d d_R^d d_R^d, \quad (7)$$

where $T$ denotes the inter-dot tunneling, and $U$ is the Coulomb interaction [22]. $d_{L(R)}^d$ creates one electron on the L (R) QD with energy $\varepsilon_{L(R)}$. The Hamiltonian of the fermionic baths (H and C) is given by

$$H_B = \sum_k \varepsilon_k \varepsilon_{kH} c_k^c c_k^t + \sum_k \varepsilon_{kC} c_{kC}^t c_{kC}^c. \quad (8)$$

The interaction between the DQD and the environment reads

$$H_I = \sum_k \left( t_{KH} c_k^t d_k^c + t_{KL} c_k^c d_k^c \right) + \sum_k \left( t_{KC} c_k^t d_k^c + t_{KC}^* c_k^c d_k^c \right), \quad (9)$$

\[\begin{align*}
\Gamma_H & \quad T \quad \Gamma_C \\
\varepsilon_L & \quad \bullet & \quad \varepsilon_R \\
\mu_H & \quad \Theta & \quad \mu_C \\
T_H & \quad \varepsilon_C & \quad T_C
\end{align*}\]

**Figure 1.** The schematic representation of a double quantum dot (DQD) system weakly coupled to two fermionic reservoirs via the rates $\Gamma_{H/C}$ (origin solid lines). The energy of the left dot (resp. the right dot) with one-electron occupation is equal to $\varepsilon_L$ (resp. $\varepsilon_R$). The electron hops between the left and right dots with internal tunneling amplitude $T$ (green solid line) and Coulomb interaction strength $U$ (red dotted line).
where \( t_{kH(C)} \) denote the coupling strengths of the transitions between the DQD and the hot (cold) electronic reservoir. The eigenstates of \( H_S \) are given by the tensorial product of the individual QD states, i.e., \(|0\rangle \) and \(|1\rangle \). In the increasing energy order, we have the four eigenstates labeled as \(|v_0\rangle = |00\rangle\), \(|v_+\rangle \sim \left[-(\Delta + \sqrt{\Delta^2 + T^2})|10\rangle + T|01\rangle\right]\), \(|v_\Delta\rangle \sim \left[-(\Delta - \sqrt{\Delta^2 + T^2})|10\rangle + T|01\rangle\right]\), and \(|v_2\rangle = |11\rangle\), where \( \Delta = (\varepsilon_R - \varepsilon_L)/2 \) and \( \varepsilon = (\varepsilon_R + \varepsilon_L)/2 \). The respective eigenvalues are \( E_0 = 0 \), \( E_- = \varepsilon - \sqrt{\Delta^2 + T^2} \), \( E_+ = \varepsilon + \sqrt{\Delta^2 + T^2} \), and \( E_2 = 2\varepsilon + U \). Using the fundamental density matrix equation describing dynamics of the DQD, we readily obtain the energy current \( I_E^{(r)} \) and the electron current \( I_M^{(r)} \) flowing into the system from the two leads (as shown in Supplementary in detail). From Eqs. (4) and (6), and Eqs. (S9) and (S10) in the Supplementary, the thermodynamic irreversibility and the optimal performances of the DQD system will be estimated.

All thermal devices between two heat reservoirs are less efficient than a reversible Carnot cycle operating between the same reservoirs. The corresponding Carnot values of reversible heat engines and refrigerators are \( \eta^C = 1 - \beta_H/\beta_C \) and \( \phi^C = \beta_H/(\beta_C - \beta_H) \), respectively. Figure 2 (a) shows that the curves of the normalized efficiency \( \eta/\eta^C \) and COP \( \phi/\phi^C \) belong to different ridges. In the left ridge, where the chemical driving force is small, the system lies in the regime suitable for heat moving from the hot side to the cold side, while the electron flow converts directly a part of heat into electricity. The system operates as a heat engine and the normalized efficiency \( \eta/\eta^C \) is shown on the plot for this range. According to Eq. (4) and Fig. 2(b), the dimensionless coupling parameter \( \zeta = 0 \) [i.e., \( I_E^{(H)}/I_M^{(H)} \to \infty \)] at \( V = V_{\eta=0} \), which is the value of the voltage at the zero efficiency [Fig. 2(a')]. The electrochemical potential gradient becomes dominant in the process of transferring electrons with the increase of the voltage and pumps the heat against the thermal gradient. Therefore, the right ridge plots the normalized COP of a refrigerator \( \phi/\phi^C \) versus \( V \). There exists a point \( V = V_{\phi=0} \) such that \( \phi/\phi^C = 0 \) and \( I_E^{(H)}/I_M^{(H)} = \mu_C \), as indicated in Eq. (6) and Fig. 2(a'). In the regions of \( V \leq V_{\eta=0} \) and \( V \geq V_{\phi=0} \), one can find a maximum efficiency \( \eta_{\text{max}}/\eta^C \) whose corresponding voltage is \( V_{\eta_{\text{max}}} \), and a maximum COP \( \phi_{\text{max}}/\phi^C \) whose corresponding voltage is \( V_{\phi_{\text{max}}} \) [Fig. 2(a')]. In the region between \( V = V_{\eta=0} \) and \( V_{\phi=0} \), the system cannot work as a heat engine or a refrigerator. The gap between refrigerator and heat engine modes in absence of tight coupling has also been observed beyond the Born–Markov approximation [23, 24].

Figures 2(a) and (b) demonstrate that the characteristics of the DQD system is inseparably related to the coupling between the energy and matter currents. The normalized efficiency and COP have perfect positive correlation with the dimensionless coupling parameter \( \zeta \). When \( I_E^{(H)}/I_M^{(H)} \) is tight coupling to the critical value \( \Theta \), given by the reservoir properties, \( \zeta \) approaches unity, and \( \eta/\eta^C \) (COP) reaches its extreme value at \( V_{\eta_{\text{max}}} \) \( (V_{\phi_{\text{max}}}) \). For the DQD system, the nonlinear relationship makes \( I_E^{(H)} \) and \( I_M^{(H)} \) unable to be zero at the same time. This difference allows \( \zeta \) to have one-sided limit that equals negative or positive infinity as \( I_E^{(H)} \) approaches 0. In the limit of a single transition channel, electron and heat flows are perfectly coupled, since every single electron carries exactly the same amount of energy. Under this circumstance, we are capable of establishing reversible electronic energy transfer between the reservoirs at the point of \( I_E^{(H)}/I_M^{(H)} = \Theta \).

The energy-matter coupling condition offers some important criteria for determining the performance of non-equilibrium systems. In order to approach the Carnot efficiency, the thermodynamic processes must be reversible and involve no change in entropy. This means that the
Carnot performance is an idealization, because no real processes are reversible. Figure 2 (c) illustrates the entropy production rate $\sigma$ as a function of the voltage $V$. Irreversible process is accompanied by the flows of matter and energy, which always results in some increase in the entropy. Figure 2(c) points out that the entropy production rate is mainly dependent upon the transition from state $|v_0\rangle$ to state $|v_+\rangle$ and from state $|v_0\rangle$ to state $|v_-\rangle$, because the population of electrons is an exponentially decreasing function of the transition energy. In the area between $V_{\eta=0}$ and $V_{\phi=0}$, $\sigma$ is actually quite small, but the device is not able to create a power and cooling cycle. The entropy production rate in term of an engine efficiency can be written as $\sigma = J^{(H)}\beta C \left[\eta^C - \eta\right]$. Obviously, when $\sigma = 0$, the efficiency $\eta$ can be shown to be equal to the Carnot limit $\eta^C$. However, $\sigma \neq 0$ for irreversible thermodynamic processes in complex systems. The working conditions of the maximum efficiency and the minimum entropy production are usually not equivalent, because the relation between $\sigma$ and $\eta$ may not be monotonic in mathematics [indicated in Figs. 2 (a) and (c)]. At the beginning, the efficiency increases with $V$. The efficiency attains its maximum at $V = V_{\eta=\max}$. In the region of $V_{\eta=0} > V > V_{\eta=\max}$, $\sigma$ and $\eta$ simultaneously decreases with $V$. In addition, it can be observed from Eqs. [2] and [4] that $\sigma$ and $\eta$ can both diminish by reducing $I^{(H)}$, when $I^{(H)}$ is constant or changes slowly. The same phenomenon could be observed in driving an irreversible Carnot refrigerator. Having a minimal amount of $\sigma$ does not mean having the largest COP.

The proper adjustment of the interaction between the energy and matter currents provides an effective way to enhance the performance of non-equilibrium systems. Figure 2(d) depicts the optimization of the efficiency and COP with respect to the energy level $\varepsilon$ and the voltage $V$. For a small $\varepsilon$, the electric field is the main driving force for the heat transfer. At this juncture, a positive thermal energy leaves the cold reservoir, and a positive thermal flux enters the hot reservoir. As $\varepsilon$ rises, heat will spontaneously travel from the hot reservoir to the cold reservoir. The DQD system allows the direct conversion of heat to electricity. A clear boundary marks an abrupt shift between the working regions of a heat engine and a refrigerator. This means that the heat engine or refrigerator cannot work in the region of the abrupt shift, i.e., $V \in \left[V_{\eta=0}, V_{\varepsilon=0}\right]$ and $\varepsilon \in \left[\varepsilon_{\phi=0}, \varepsilon_{\eta=0}\right]$, where $\varepsilon_{\phi=0}$ is the value of $\varepsilon$ at the zero COP and $\varepsilon_{\eta=0}$ is the value of $\varepsilon$ at the zero efficiency. We also observed that the more the coupling parameter $I^{(H)}_{I^{(H)}}$ approaches $\Theta$ for a given QD energy level, the better the performance of the heat engine and refrigerator (Section 3 in Supplementary). In a practical design, we should make our best effort to match the energy-matter coupling condition. When $\varepsilon >> U$ and $\varepsilon >> T$, all electrons are tunneling at energy $\varepsilon$. One then recovers the optimal performance approaching Carnot efficiency or COP [as indicated in Fig. 2 (d)], because the system behaves like a thermo-electric machine consisting of a single quantum level [3, 12, 15]. Similar phenomena can also be observed under the condition that the inter-dot tunneling amplitude and the electrostatic force are incredibly larger than the QD energy levels, where the two lowest electronic states $|v_0\rangle$ and $|v_-\rangle$ govern the carrier excitation.

In summary, based on the entropy production rates of far-from-equilibrium open systems, we prove that the energy conversion performances of these systems can be improved by suitably adjusting the coupling strengths between the energy and matter currents. We apply the theory to a DQD system that is weakly coupled to two separate electronic reservoirs and attain its performance upper bound. The results show that the universal thermodynamic coupling rule can open a new field in the application of nano-devices.

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