Carnot Efficiency and Zero-Entropy Production Rate Do Not Guarantee Reversibility of a Process

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A thermodynamic process at a zero-entropy production (EP) rate has been regarded as a reversible process. A process achieving the Carnot efficiency is also considered a reversible process. Therefore, the condition, ‘Carnot efficiency at zero-EP rate’ can be regarded as a strong condition for a reversible process. Here, however, we show that the detailed balance can be broken for a zero-EP rate process and even for a process achieving the Carnot efficiency at a zero-EP rate in an example of a quantum-dot model. This clearly demonstrates that ‘Carnot efficiency at zero-EP rate’ or just ‘zero-EP rate’ is not a sufficient condition for a reversible process.

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1. INTRODUCTION

A reversible process is a process that its reversed one returns the system to the initial state without leaving any trace in the environment. Therefore, in a reversible process, every transition should be equilibrated by its reverse transition, which is called a detailed balance (DB). If the DB is satisfied, no current can flow. In addition, no entropy is produced in a DB-satisfied process, as the entropy production (EP) can be defined by the logarithmic ratio between the forward and its time-reversal path probabilities [1].

As a system should always be maintained in an equilibrium state during the process, an infinitely long time is required to implement the process in an exactly reversible way. However, such an infinite-time process does not exist in the real world. Therefore, a reversible process is usually understood as a quasi-static-limit (very slowly varying) process for practical purposes. In this limit, all currents, including the EP rate, should vanish. Therefore, in this context, the ‘zero-EP rate’ limit has been usually and practically regarded as an equivalent condition for the reversible limit. In this work, we will show that this conventional belief does not apply in some limiting processes.

If we focus our discussion on heat engines working between two reservoirs at temperatures $T_1$ and $T_2$ ($T_1 > T_2$), another conventional indicator for reversibility exists: that is, how close the engine efficiency is to the Carnot efficiency $\eta_C = 1 - T_2/T_1$. This ideal efficiency is attainable in a reversible process as in the well-known Carnot engine [2]. This can be easily understood by the following relation for the efficiency $\eta$ and the total EP per engine cycle $\Delta S$ [3]:

$$\eta_C - \eta = \frac{T_2 \Delta S}{Q_1},$$

where $Q_1$ is the amount of heat absorbed from the hotter reservoir per engine cycle. From Eq. (1), obviously, $\eta$
approaches $\eta_C$ in the $\Delta S \to 0$ (reversible) limit. On the other hand, for $\Delta S > 0$ (irreversible process), $\eta$ should be lowered as much as $T_2 \Delta S / Q_1$. For this reason, the limit achieving $\eta_C$ has been considered to be equivalent to the reversible limit. However, note that reversibility may not be required in achieving $\eta_C$ when $Q_1 \to \infty$.

For a steady-state engine, Eq. (1) can be written as

$$\eta_C - \eta = \frac{T_2 \dot{S}}{Q_1},$$

where $\dot{Q}_1$ and $\dot{S}$ are the steady-state rates of $Q_1$ and $S$, respectively. In the reversible limit, $\dot{S}$ approaches zero, and the Carnot efficiency is attained. Therefore, the $\dot{S} \to 0$ limit has been also regarded to guarantee the Carnot efficiency. Again, however, this may not be correct in some limits such as $\dot{Q}_1 \to 0$. Furthermore, the $\dot{S} \to 0$ limit does not always guarantee reversibility in the sense of the DB satisfiability.

This can be understood in a simple way as follows: The EP ($\Delta S$) during a characteristic time $\tau$ can define the EP rate in the steady state as $\dot{S} = \Delta S / \tau$. If the DB is satisfied, $\Delta S$ for any finite time interval should vanish. Thus, the DB always guarantees the zero-EP rate. However, the other way around is not always true in the $\tau \to \infty$ (slow dynamics) limit. This limit can be quite non-trivial such that $\Delta S$ can be finite or even weakly diverging ($\Delta S \sim \tau^\alpha$ with $0 < \alpha < 1$), still with vanishing $\dot{S}$. Non-zero $\Delta S$ implies a broken DB, thus irreversibility. We study various non-trivial limits analytically through a simple quantum-dot model and discuss the feasibility of these limits in real experiments.

Recently, several researchers motivated by studies on the Carnot efficiency at finite power [4–8] pointed out that the conventional belief could be wrong by studying explicit models violating the equivalence [3, 9, 10]. Lee and Park [3] showed that the efficiency of the Feynman-Smoluchowski ratchet [11, 12] can approach the Carnot bound with non-vanishing $\Delta S$ (DB violation) in a specific limit. In this ratchet model, the system should overcome a steep hill of the periodic energy barrier with height $U$ to extract work. They found that $\Delta S \propto \ln U$ and $Q_1 \propto U$ when the system overcomes the energy barrier once (one hopping). Therefore, in the $U \to \infty$ limit, the Carnot efficiency is attainable from Eq. (1). However, as it takes a typical time duration $\tau \sim e^U$ to overcome the barrier, the EP rate vanishes as $e^{-U} \ln U$ ($\dot{S} \to 0$). This limit is peculiar in that positive entropy is produced when overcoming an energy barrier, but all currents, including the EP rate, vanish due to the exponentially slow process. As vanishing currents are also key features in a reversible process, some confusion existed on whether this process should be classified as an irreversible or a reversible one. To clear up the ambiguity in determining the reversibility, one should examine the DB satisfiability in the steady state; if the DB is broken, the process cannot be reversible [13]. The DB turns out not to hold in this limit with the zero-EP rate and the Carnot efficiency, which clearly shows that the conventional belief of the equivalence does not hold.

Polettini and Esposito [10] showed that the Carnot efficiency could be attained at a divergent power output in a two-cycle model. In this limit, both $\dot{S}$ and $\dot{Q}_1$ diverge while the ratio $\dot{S} / \dot{Q}_1$ vanishes; thus, the efficiency approaches $\eta_C$ by Eq. (2). This confirms that the Carnot efficiency limit guarantees neither zero-EP rate nor reversibility.

In this work, we study the relationship between $\dot{S} \to 0$, $\eta \to \eta_C$, and the reversibility (DB satisfaction) in a systematic way. This is a generalization of our previous work [3] to a general and simpler setup. The reversibility condition, of course, guarantees the two other limits of $\dot{S} \to 0$ and $\eta \to \eta_C$. Then, the most general logical Venn diagram for the three limits can be drawn as in Fig. 1, which suggests four possible cases: (i) Region I: The EP rate vanishes without the Carnot efficiency. (ii) Region II: The Carnot efficiency is attained with non-vanishing EP rate, which is negligible as compared to power. The models studied by Polettini and Esposito [10] and also by Holubec and Ryabov [14, 15] belong to this region. (iii) Region III: A process is irreversible even when both $\dot{S} \to 0$ and $\eta \to \eta_C$ are satisfied. Therefore, the ‘Carnot efficiency at zero EP rate’ does not guarantee a reversible process. The Feynman-Smoluchowski ratchet [3] is one such example. A similar behavior was also observed in other systems, such as a quantum refrigerator [9]. (iv) Region IV: All three limits are realized simultaneously, which corresponds to the conventional belief.

II. QUANTUM-DOT MODEL

To demonstrate our conclusion shown in Fig. 1, we consider the thermoelectric device [16–18] illustrated in Fig. 2. This device consists of a quantum dot in contact with two leads or reservoirs with different temperatures $T_1$ and $T_2$ and different chemical potentials $\mu_1$ and $\mu_2$, respectively. Electrons can move from one reservoir to another via the quantum dot where only a single electron can occupy a state with a sharply defined energy $E$. Thus, two states of the dot, occupied and unoccupied states whose energies are $E$ and 0, respectively, are
possible.

In this study, we consider the case $T_1 > T_2$ and $\mu_1 < \mu_2 < E$. The transition rate of an electron from lead 1 (2) to the dot is $q$ ($\bar{q}$) and the corresponding reverse rate is $\bar{q}$ ($q$). Then, this system can be described by the following master equations [16,18–21]:

\[
\begin{align*}
\dot{P}_{oc} &= (q + \bar{\epsilon})P_{un} - (\bar{q} + \bar{\epsilon})P_{oc}, \\
\dot{P}_{un} &= (\bar{q} + \bar{\epsilon})P_{oc} - (q + \bar{\epsilon})P_{un},
\end{align*}
\]

(3)

where $P_{oc}$ and $P_{un}$ are the probabilities of occupied and unoccupied states of the quantum dot, respectively. Here, we assume the local detailed balance conditions for the transition rates such that

\[
q = e^{-(E - \mu_1)/T_1} \equiv x, \quad \bar{q} = e^{-(E - \mu_2)/T_2} \equiv y, \quad \bar{\epsilon} = e^{-(E - \mu_2)/T_2} \equiv \bar{y}, \quad q = e^{-(E - \mu_1)/T_1} \equiv \bar{x}, \quad \bar{q} = e^{-(E - \mu_2)/T_2} \equiv \bar{y},
\]

(4)

(5)

where we set the Boltzmann constant $k_B = 1$ for convenience. For simplicity, we take the time constants for the transition rates as $q + \bar{q} = \epsilon + \bar{\epsilon} = 1$. Then, the steady-state solution of Eq. (3) is given by

\[
\begin{align*}
P_{ss_{oc}} &= \frac{1}{2}(q + \epsilon) = 1 - P_{ss_{un}}, \\
P_{ss_{un}} &= \frac{1}{2}(\bar{q} + \bar{\epsilon}) = \frac{x - y}{2(1 + x)(1 + y)}. \quad (6)
\end{align*}
\]

We note that the DB condition for the probabilistic current balance between the quantum dot and each lead reads as

\[
\frac{qP_{ss_{un}}}{P_{ss_{oc}}} = \frac{\bar{q}P_{ss_{oc}}}{\bar{\epsilon}P_{ss_{un}}} = 1 \quad \iff \quad x = y \quad \text{(DB condition)}, \quad (7)
\]

with which we get $J^{ss} = 0$ trivially.

As energy and matter are strongly coupled in this model, the steady-state heat currents are given as follows:

\[
\begin{align*}
\dot{Q}_1 &= J^{ss}(E - \mu_1) = -J^{ss}T_1 \ln x, \\
\dot{Q}_2 &= J^{ss}(E - \mu_2) = -J^{ss}T_2 \ln y,
\end{align*}
\]

(8)

(9)

(10)

where $\dot{Q}_1$ ($\dot{Q}_2$) is the heat current from lead 1 (2) to the dot, respectively. Then, the work rate is the difference between the two heat currents:

\[
\dot{W} = \dot{Q}_1 - \dot{Q}_2 = J^{ss}(T_2 \ln y - T_1 \ln x). \quad (11)
\]

By definition, positive $\dot{W}$ means useful work extraction as an engine. Using Eqs. (9) and (10), we can calculate the EP rate $\dot{S}$ and the efficiency $\eta$ as

\[
\begin{align*}
\dot{S} &= \frac{\dot{Q}_2}{T_2} - \frac{\dot{Q}_1}{T_1} = J^{ss}(\ln x - \ln y), \\
\eta &= \frac{\dot{Q}_2/Q_1}{\dot{Q}_2} = 1 - \frac{T_2 \ln y}{T_1 \ln x}.
\end{align*}
\]

(12)

(13)

III. VARIOUS LIMIT PROCESSES

Two constraints for $x$ and $y$ exist: (i) From the thermodynamic second law, $\dot{S} \geq 0$ and (ii) for being an engine, $\dot{W} \geq 0$. These two constraints are summarized as

\[
x^{T_1/T_2} < y \leq x, \quad (14)
\]

and the corresponding region is shaded in Fig. 3. The lower bound ($y = x^{T_1/T_2}$) corresponds to $\dot{W} = 0$ ($\mu_1 = \mu_2$), $\eta = 0$, $J^{ss} > 0$ and $\dot{S} > 0$, and the upper bound ($y = x$) corresponds to equilibrium with $J^{ss} = 0$ and, thus, $\dot{S} = \dot{W} = \dot{Q}_1 = \dot{Q}_2 = 0$.

We first consider a simple limit to reach the equilibrium line ($y = x$) for fixed nonzero $x$. This can be realized by varying $\mu_2$ close to $\mu_1 + \eta C (E - \mu_1)$ with fixed $E$ and $\mu_1$. This is the reversible limit, where $\eta \rightarrow \eta_C$ and $\dot{S} \rightarrow 0$ with the DB condition in Eq. (8) satisfied. In fact, any linear or nonlinear approach to the equilibrium line except for the origin ($x = y = 0$) turns out to be the reversible limit (Region IV).

However, various limits can approach the origin, where the energy gap $E - \mu_1$ ($E - \mu_2$) is much higher than the thermal energy $T_1$ ($T_2$), respectively (see Eqs. (4) and (5)). For example, if one approaches the origin along the equilibrium line, the process is maintained as a reversible process with the Carnot efficiency (Region IV). The other simple limit is obtained by taking the lower-bound line ($y = x^{T_1/T_2}$) in Fig. 3. Along this line, the efficiency is always zero ($\eta = 0$), and the DB is always broken ($x \neq y$). The EP rate $\dot{S}$ vanishes as one approaches the origin because $J^{ss}$ vanishes faster, even
In Fig. 4(a), $\dot{J}$ Eqs. (7), (11), (12), and (13) that temperatures. In this limit, one can see easily from by tuning both energy gaps appropriately with fixed $0 < a < 1$, as illustrated in Fig. 3. This can be achieved through controlling the gate voltage connected to the quantum dot with fixed $\mu_1$ and $\mu_2$ [17]. The results are similar to the simple lower-bound line case ($c = 1$) such that $J^{ss} \rightarrow 0$, $W \rightarrow 0$, $\dot{S} \rightarrow 0$, and $\eta \rightarrow 0$. The probability current ratios in this case $r_q \rightarrow 2$ and $r_c \rightarrow 0$ (broken DB); thus, this limit belongs to Region I with diverging $\Delta S$. Figure 4(b) shows plots of various quantities when $c = 2$, $T_1 = 1$, and $T_2 = 1/3$. We note an interesting anomalous behavior in that ‘the larger the irreversibility is, the higher the efficiency (or higher power) is’. Usually, the efficiency or power decreases as the EP rate increases. However, in the blue shaded region of Fig. 4(b), we can see the opposite behavior, which was also reported previously in the Feynman-Smoluchowski ratchet [3]. For a general path limit with $y \sim x^n$, we find that $J^{ss} \rightarrow 0$, $W \rightarrow 0$, $\dot{S} \rightarrow 0$, and $\eta \rightarrow 1 - (1 - \eta_C)\alpha$ with $r_q \rightarrow 2$, $r_c \rightarrow 0$, and $\Delta S \rightarrow \infty$, which belongs to Region I.

The mechanism of this abnormal behavior is as follows: As mentioned before, the EP rate can be factorized into two terms: $J^{ss}$ and $\Delta S$, that is, $\dot{S} = J^{ss}\Delta S$ from Eq. (15). With the DB satisfied, the EP is always zero by definition ($\Delta S = 0$); thus $\dot{S} = 0$, which is the usual reversible limit. However, one can reach the zero-EP rate with the DB violated ($\Delta S \neq 0$) when the engine is operated so slowly that $J^{ss}$ vanishes in some limits. This case generally belongs to Region I.

In some special cases, the efficiency may also reach
the Carnot efficiency when the EP rate vanishes significantly faster than the heat absorption rate, \( \dot{S} \ll \dot{Q}_1/T_2 \) (see Eq. (2)). This case belongs to Region III and was found in the linear limit of the quantum-dot model with non-zero finite \( \Delta S \) and diverging \( Q_1 \equiv \dot{Q}_1/J = ^{\prime} (\text{heat absorbed per one-electron transfer}) \) in Eq. (9). This mechanism is essentially the same as what was found in a previous work [3], where \( \Delta S \) was also diverging, but weaker (logarithmic divergence) than \( Q_1 \) (linear divergence), with increasing energy barrier height.

IV. CONCLUSION

In summary, we demonstrate that (i) the zero-EP rate limit does not guarantee the ideal efficiency or reversibility and (ii) the Carnot efficiency can be approached at zero-EP rate in an irreversible process. Using a simple quantum-dot model, we find that such a limit can be achieved by properly increasing the energy of the quantum dot or the chemical potentials. The \( \dot{S} \to 0 \) and \( \eta \to \eta_C \) limit is also consistent with the recently proven power-efficiency trade-off relations [22–24], in that the power vanishes with the Carnot efficiency.

Finally, we add a comment about an experiment with the quantum-dot model. The quantum-dot model was experimentally implemented by using the setup studied by Josefsson et al. [17]. In this experiment, the charging energy of the quantum dot was 4.9 meV at \( T_1 = 2 \text{ K} \) (corresponding thermal energy was 0.17 meV). Thus, \( x \) can be reduced to \( \sim e^{-4.9/0.17} \approx 3.0 \times 10^{-13} \). If we take \( T_2 = 1 \text{ K} \) and \( a = 1/e \), the normalized efficiency \( \tilde{\eta} \) becomes 0.97 with vanishing EP rate and broken DB. Therefore, the limits considered in this work could be accessible in the real experiments. We note that in this setup \( \Delta S = 1, Q_1 = -T_1 \ln x = 58 \text{ K}, Q_2 = -T_2 \ln y = 30 \text{ K}, W \equiv Q_1 - Q_2 = 28 \text{ K}. \) Thus, \( \Delta S \ll Q_1/T_2 \) is satisfied.

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