PHYSICAL REVIEW E **92**, 050101(R) (2015)

Attainability of Carnot efficiency with autonomous engines

Naoto Shiraishi
Department of Basic Science, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan
(Received 6 July 2015; revised manuscript received 30 October 2015; published 30 November 2015)

The maximum efficiency of autonomous engines with a finite chemical potential difference is investigated. We show that, without a particular type of singularity, autonomous engines cannot attain the Carnot efficiency. This singularity is realized in two ways: single particle transports and the thermodynamic limit. We demonstrate that both of these ways actually lead to the Carnot efficiency in concrete setups. Our results clearly illustrate that the singularity plays a crucial role in the maximum efficiency of autonomous engines.

DOI: 10.1103/PhysRevE.92.050101 PACS number(s): 05.70.Ln, 05.40.−a, 87.10.Mn, 87.16.Nn

Introduction. The maximum efficiency of heat engines has been one of the central issues in thermodynamics. Carnot showed that the efficiency of an engine attached to heat baths with temperature T_H and T_L $(T_H > T_L)$ is bounded by $1 - T_L/T_H$ [1]. The upper bound is attained when the external control on the engine is quasistatic. For the case with two particle baths under isothermal conditions, the efficiency is bounded by 1. These maximum efficiencies are called the Carnot efficiency (CE). Nonequilibrium thermodynamics has recently been applied to small fluctuating systems with external control, where the maximum efficiency analogous to macroscopic thermodynamics has been established [2].

Since most engines, from electric power plants to molecular motors, are autonomous, thermodynamics for autonomous engines is an important issue. Here, the word *autonomous* stands for systems with no time-dependent control parameter in nonequilibrium steady states [3]. Since all variables of the engine inevitably fluctuate, the attainability of the CE with autonomous engines is a nontrivial problem. In the linear response regime (i.e., $T_H - T_L \simeq 0$), it is well known that the tight-coupling condition is necessary for autonomous engines to attain the CE [4]. On the other hand, for the case of a finite difference of temperatures or chemical potentials, most of the studies have paid attention to specific and elaborated models [5–27]. Famous models of autonomous engines are Feynman's ratchet [5] and the Büttiker-Landauer system [6,7], which convert heat flux into work. Although they seemingly attain the CE [5,8], it has been established that these models actually cannot attain the CE in physically plausible setups [9–12]. Another famous model is an information engine [13–16], which performs autonomous control and always transports a single particle between particle baths. In contrast to Feynman's ratchet and the Büttiker-Landauer system, the information engine attains the CE. In addition, limiting effective filters of energy or chemical potential [17–21], a quantum dot [22,23], and soft nanomachines [24] also attain the CE. However, contrary to externally controlled engines, a comprehensive understanding of autonomous engines with a finite difference of temperatures or chemical potentials has been elusive. Especially, the understanding of macroscopic autonomous engines is missing.

In this Rapid Communication, we address the issue of the general condition for autonomous engines to attain the CE with a finite chemical potential difference. To demonstrate this, we first introduce a schematic model, an autonomous version of the macroscopic Carnot engine. This model clearly illustrates the characteristics of autonomous engines that in normal nonsingular setups they cannot attain the CE, even with infinitely slow dynamics. Contrary to this, in the case of singular transition rates, since this singularity prohibits a particle leakage from the dense bath to the dilute bath, this engine attains the CE. We then move to a general discussion and prove that, without a special type of singularity, any autonomous engine cannot attain the CE, which is consistent with both our model and the existing models [5–27].

Kinetic model and its coarse graining. It is hard for autonomous engines to attain the CE, and they attain the CE only if they possess a special type of singularity. To demonstrate the above characteristics of autonomous engines, we introduce an autonomous Carnot engine, which extracts mechanical work from a particle flux between particle baths with given chemical potentials μ_H and μ_L. The engine consists of two movable walls, a V wall and H wall [see Fig. 1(a)]. Only when the H wall (V wall) is at the position t or b (l or r), the V wall (H wall) can move along the x (y) axis, otherwise the V wall (H wall) is fixed at l or r (t or b) [see Fig. 1(b)]. Thus, the engine has four stable positions, (l,b), (l,t), (r,t), and (r,b), which we denote by A, B, C, and D, respectively. When the V wall is at the position l (r), the engine can exchange particles with the bath with μ_H (μ_L). Otherwise, the engine cannot exchange particles. The engine is under isothermal conditions, and the dynamics of the walls and particles are stochastic (the explicit time-evolution equation is shown in Ref. [28]). Since the cross point of two walls passes through the rectangular-shaped trajectory $A \to B \to C \to D \to A$, by imposing torque on the cross point, we extract mechanical work automatically [see Fig. 1(c) and Fig. S1].

Here, we adopt a well-used approximation that, with a given position of the walls and particle number, the particles are in equilibrium [29,30]. If the equilibration of particles is much faster than the dynamics of the walls and the exchange of particles with the baths, the above approximation is justified. This time separation leads to a coarse-grained description, the Markov jump processes with discrete states (X,n), where $X \in \{A,B,C,D\}$ represents the position of the walls and n represents the particle number. We call this model a coarse-grained autonomous Carnot engine (CGACE).

The energy difference from A to B including the external force is denoted by E_{AB}, and E_{BC}, E_{CD}, and E_{DA} are defined in a similar manner. Then the work against the imposed force per one rotation $A \to B \to C \to D \to A$ is written as $E_{AB} + E_{BC} + E_{CD} + E_{DA} =: W_{\mathrm{tot}} > 0$. Since the engine is under

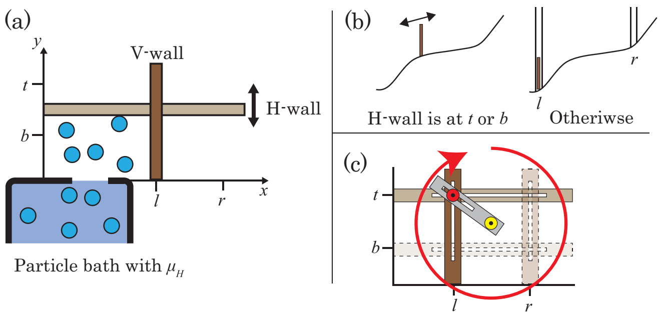

FIG. 1. (Color online) (a) Schematic of the autonomous Carnot engine, which consists of a V wall and H wall. Since the V wall is at l, particles can be exchanged with the particle bath with μ_H. (b) The potential landscape of the V wall. If the H wall is at t or b, the V wall is movable. Otherwise, the V wall is trapped at l or r by delta-function-type potentials. (c) Schematic of the torque. The red disk is on the cross point of the V wall and H wall, which slides on both walls. The yellow disk is fixed and serves as a shaft of the gray slat. With a single rotation $A \to B \to C \to D \to A$, the gray slat makes one rotation and we extract mechanical work.

isothermal conditions, the transition rates of the V wall (i.e., $A \leftrightarrow D$ and $B \leftrightarrow C$) should satisfy the local detailed balance condition,

$$\ln \frac{P(X \to X^-;n)}{P(X^- \to X;n)} = -\beta(E_{XX^-} + F(V_{X^-},n) - F(V_X,n)), \tag{1}$$

where we defined $A^- := D$, $B^- := C$, $C^- := B$, $D^- := A$, and $E_{XX^-} := -E_{X^-X}$, and $\beta = 1/k_B T$ is the inverse of the Boltzmann constant times temperature. $P(X \to X^-;n)$, V_X, and $F(V,n)$ represent the transition rate from (X,n) to (X^-,n), the volume at X, and the Helmholtz free energy with volume V and particle number n, respectively. Note that the details of the transition rates of the H wall as $P((A,n) \to (B,n'))$ are not important in the following discussion.

Maximum efficiency of CGACE. To confirm the difficulty for autonomous engines to attain the CE, here we derive the maximum efficiency of the CGACE with fixed μ_H and μ_L. In the following, we investigate the condition for the maximum efficiency, and then calculate the efficiency under this condition. First, an engine with maximum efficiency should prevent two kinds of leakage. One is the leakage of particles: If the dynamics of the H wall is very slow, the V wall moves between $B \leftrightarrow C$ or $A \leftrightarrow D$ many times and particles leak from the dense bath to the dilute bath without extracting work. The other is the leakage of energy: If the exchange of particles between the baths and the engine is very slow, the walls rotate, obeying the external force as $A \to D \to C \to B \to A$, and the work is lost. Hence, it is plausible that the maximum efficiency is realized when the dynamics of the V wall is much slower than that of the H wall and particles, and we treat this situation in the following.

The stationary distribution $P_{st}(B,n)$, for example, is then calculated as

$$P_{st}(B,n) = P_{st}(A,B)\frac{e^{-\beta(F(V_B,n)+E_{AB}-\mu_H n)}}{Z_{AB}}, \tag{2}$$

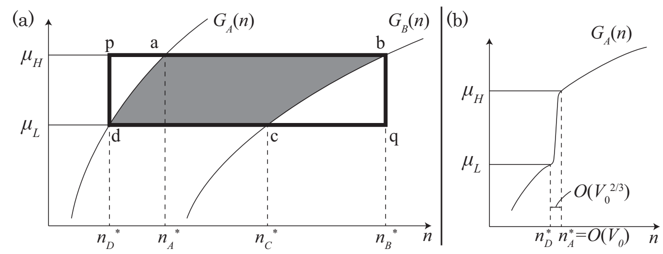

FIG. 2. (a) Graphs of $G_A(n)$ and $G_B(n)$. The area of "abcd" (colored by gray) corresponds to the right-hand side of Eq. (5), which is the upper bound for W_{tot}. The area of "pbqd" (surrounded by bold lines) corresponds to the lower bound for C_μ. (b) A graph of $G_A(n)$ with singular transition rates (9) and (10). G_A shows almost discontinuous behavior, which allows n_A^* and n_D^* as $n_A^* - n_D^* = O(V_0{}^{2/3})$.

where $P_{st}(A,B)$ represents the stationary probability at A or B, and $Z_{AB} := \sum_n e^{-\beta(F(V_A,n)-\mu_H n)} + e^{-\beta(F(V_B,n)+E_{AB}-\mu_H n)}$ is a normalization constant. We denote the stationary probability flux of $X \to X^-$ with n particles by $j_{X\to X^-}(n) := P_{st}(X,n)P(X \to X^-;n)$. Owing to the law of large numbers, the realized particle number when the transition $X \to X^-$ occurs is around $n_X^* := \arg\max_n j_{X\to X^-}(n)$.

We now calculate the efficiency $\eta := W_{tot}/C_\mu$, where C_μ represents the average consumption of the chemical potential per a single rotation $A \to B \to C \to D \to A$. The condition that the direction of the dominant dynamics of the walls is $A \to B \to C \to D \to A$ leads to

$$j_{A\to D}(n_A^*) < j_{D\to A}(n_D^*), \tag{3}$$

$$j_{C\to B}(n_C^*) < j_{B\to C}(n_B^*). \tag{4}$$

Summing the logarithms of (3) and (4), and using the local detailed balance condition (1), we arrive at a key inequality:

$$W_{tot} < \left(\mu_H n_B^* - \mu_L n_C^* - \int_{n_C^*}^{n_B^*} G_B(n)dn\right) - \left(\mu_H n_A^* - \mu_L n_D^* - \int_{n_D^*}^{n_A^*} G_A(n)dn\right). \tag{5}$$

Here, $G_X(n)$ $(X = A,B)$ is defined as

$$G_X(n) := \frac{\partial}{\partial n}\left(F(V_X,n) - \frac{1}{\beta}\ln P(X \to X^-;n)\right), \tag{6}$$

and n_X^* satisfies $G_A(n_A^*) = G_B(n_B^*) = \mu_H$ and $G_B(n_C^*) = G_A(n_D^*) = \mu_L$. Note that the second law of thermodynamics implies a monotonic increase of $G_X(n)$. The right-hand side (rhs) of (5) corresponds to the area of "abcd" (colored by gray) in Fig. 2(a). In addition, C_μ is evaluated as $C_\mu \geqslant (\mu_H - \mu_L)(n_B^* - n_D^*)$, whose rhs corresponds to the area of "pbqd" (surrounded by bold lines) in Fig. 2(a). If a finite constant $a < +\infty$ satisfies

$$n\frac{\partial G_A}{\partial n} \leqslant a, \quad n\frac{\partial G_B}{\partial n} \leqslant a \tag{7}$$

for any n, the inequality (5) implies

$$\eta := \frac{W_{tot}}{C_\mu} \leqslant \frac{a(1-e^{-\beta\Delta\mu/a})}{\beta\Delta\mu} < 1 = \eta_{Carnot}, \tag{8}$$

where we used $G_A(n) \leqslant a \ln(n/n_D^*) + \mu_L$ for $n \geqslant n_D^*$ and $G_B(n) \geqslant a \ln(n/n_B^*) + \mu_H$ for $n \leqslant n_B^*$. The inequality (8) indicates that the maximum efficiency of the CGACE is strictly less than the CE. Especially, if the transition rates of the V wall obey the symmetric rule [31] or the Arrhenius rule [32], the condition (7) is equivalent to the condition for the thermodynamic function of the gas: $\sup_{n,V} n\, \partial^2 F/\partial n^2 \leqslant a$. We note that the ideal gas satisfies $n \cdot \partial^2 F/\partial n^2 = \beta$ for any n and V.

In the foregoing discussion, it was shown that the CGACE cannot attain the CE with normal transition rates. However, the CGACE attains the CE with the transition rate with a special type of singularity. We again assume that the dynamics of the V wall is much slower compared to the H wall and the particle exchange. We set the transition rates between A and D as

$$P(A \to D; n) = \frac{k\, e^{-\beta(F(V_D,n)-E_{DA})}}{e^{-\beta F(V_A,n)} + e^{-\beta(F(V_D,n)-E_{DA})}}, \tag{9}$$

$$P(D \to A; n) = \frac{k\, e^{-\beta F(V_A,n)}}{e^{-\beta F(V_A,n)} + e^{-\beta(F(V_D,n)-E_{DA})}}, \tag{10}$$

with a constant k. The transition rates $P(B \to C; n)$ and $P(C \to B; n)$ are also written in a similar manner with the same k. We note that such transition rates are physically realizable [28].

The crucial point of the form of $P(A \to D; n)$ is that G_A shows an almost discontinuous jump from μ_L to μ_H [see Fig. 2(b)]. This discontinuity leads to the divergence of $n\, \partial G_A/\partial n$, and thus the left-hand side of the inequality (8) does not prohibit the attainability of the CE. We then properly set $V_A, V_B, V_C, V_D = O(V_0)$ and $E_{AB}, E_{BC}, E_{CD}, E_{DA} = O(V_0)$ as satisfying $n_A^* - n_D^* = O(V_0^{2/3})$ and $n_B^* - n_C^* = O(V_0^{2/3})$, which are negligible in thermodynamic limits. Under this setup, the efficiency is evaluated as

$$\eta := \frac{W_{\mathrm{tot}}}{C_\mu} \geqslant 1 - O\left(\frac{1}{V_0^{1/3}}\right), \tag{11}$$

which indicates the attainability of the CE with the thermodynamic limit $V_0 \to \infty$ (detailed setups and calculations are discussed in Ref. [28]).

Necessary condition to attain the CE. We now leave the specific model and go to the argument on general autonomous engines with a finite chemical potential difference, which includes models in Refs. [5–27]. We note that if the engine has continuous variables, we take their proper discretization. We also note that our argument for particle baths is easily extended to the case of thermal baths. By adding a new stochastic parameter if necessary [28], an autonomous engine satisfies the following two conditions: (a) The engine touches at most one particle bath at one moment. (b) The energy difference of the engine between two states (as E_{XX^-} in the CGACE) is independent of its particle number n. We then divide the possible states of the engine into $\{X_{1,H}, \ldots, X_{n,H}\}$ and $\{X_{1,L}, \ldots, X_{m,L}\}$, where a state $X_{i,H}$ ($X_{i,L}$) is attached to the bath with μ_H (μ_L) [see Fig. 3(a) or Fig. S1]. The state of the whole system is written as (X, n). In the case of the CGACE, the engine takes four possible states $\{A, B\} = \{X_{1,H}, X_{2,H}\}$ and $\{C, D\} = \{X_{1,L}, X_{2,L}\}$. In the case of the (discretized) Büttiker-Landauer system [6–8,12], X_H (X_L) corresponds to the position of the Brownian particle attached to a hot (cold) bath [see Fig. 3(b)].

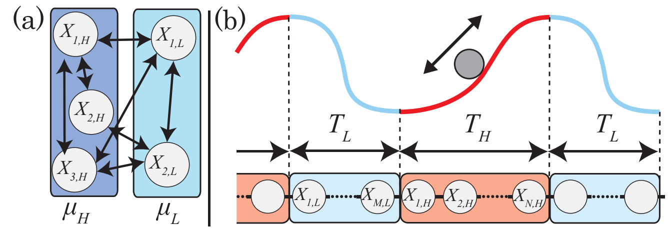

FIG. 3. (Color online) (a) An instance of the state space of an engine. $X_{1,H}, X_{2,H}, X_{3,H}$ touches the particle bath with μ_H, and $X_{1,L}, X_{2,L}$ touches the particle bath with μ_L. Arrows represent possible transitions. (b) Schematic of the (discretized) Büttiker-Landauer system and its state space. $X_{i,H}$ ($X_{i,L}$) represents the position of the Brownian particle with a hot (cold) bath. The whole state of the system is determined by the position X, the energy E, and the direction of the motion $c \in \{+,-\}$.

Here, we use the fact that a thermodynamic engine which attains the CE satisfies the detailed balance condition [33], which is a consequence of the widely believed conjecture that thermodynamic engines with the CE move quasistatically, and which has recently been proved for Markovian systems [34]. Then, the stationary distribution for n with given X reduces to a grand canonical distribution. Hence, the average of the particle number transported from $X_{i,H}$ to $X_{j,L}$ per unit time is calculated as

$$\langle n \rangle_{X_{i,H} \to X_{j,L}} = \sum_n \frac{n f(n) e^{\beta \mu_H n}}{\sum_{n'} f(n') e^{\beta \mu_H n'}}, \tag{12}$$

where we defined $f(n) := e^{-\beta F(X_{i,H},n)} P(X_{i,H} \to X_{j,L}; n)$. By assuming the local detailed balance condition for X, $\langle n \rangle_{X_{j,L} \to X_{i,H}}$ is calculated in a similar manner:

$$\langle n \rangle_{X_{j,L} \to X_{i,H}} = \sum_n \frac{n f(n) e^{\beta \mu_L n}}{\sum_{n'} f(n') e^{\beta \mu_L n'}}. \tag{13}$$

Here, we used the fact that the local detailed balance condition is written in a similar manner to Eq. (1), which follows from condition (b).

Let V_0 be a typical system size. Since the amount of extracted work is of order V_0, the necessary condition for the absence of particle leakage between $X_{i,H}$ and $X_{j,L}$ is

$$\frac{1}{V_0}\left(\langle n \rangle_{X_{i,H} \to X_{j,L}} - \langle n \rangle_{X_{j,L} \to X_{i,H}}\right) = 0. \tag{14}$$

However, by comparing Eqs. (12) and (13), a monotonic increase of $e^{\beta(\mu_H - \mu_L)n}$ in terms of n yields

$$\frac{1}{V_0}\left(\langle n \rangle_{X_{i,H} \to X_{j,L}} - \langle n \rangle_{X_{j,L} \to X_{i,H}}\right) \geqslant 0, \tag{15}$$

and the equality holds only when $f(V_0 \rho) e^{\beta \mu_L V_0 \rho}$ has a delta-function-type singularity in terms of $\rho := n/V_0$, such that

$$j_{X_{i,H} \to X_{j,L}}(V_0 \rho) \propto f(V_0 \rho) e^{\beta \mu_H V_0 \rho} \propto \delta(\rho - \rho^*), \tag{16}$$

$$j_{X_{j,L} \to X_{i,H}}(V_0 \rho) \propto f(V_0 \rho) e^{\beta \mu_L V_0 \rho} \propto \delta(\rho - \rho^*). \tag{17}$$

Here, $j_{X\to X'}(n)$ represents the probability flux of $X \to X'$ with particle number n. Note that ρ is not the particle density. The conditions (16) and (17) have a clear physical meaning: Particle numbers with both transitions $X_{i,H} \to X_{j,L}$ and $X_{j,L} \to X_{i,H}$ are always the same unique value $V_0\rho^*$ within $o(V_0)$, which is the only way to prevent the leakage of particles. Since μ_H and μ_L are fixed, this singularity appears in two ways: (i) $P(X_{i,H} \to X_{j,L}; n) = 0$ for all $n \in \mathbb{N}$ except $n = V_0\rho^*$. (ii) $1/V_0 \cdot \partial/\partial\rho \ln f(V_0\rho)$ shows such discontinuity that

$$\lim_{\rho'\to\rho^*-0} \lim_{V_0\to\infty} \frac{1}{V_0}\frac{\partial}{\partial\rho} \ln f(V_0\rho)\bigg|_{\rho=\rho'} \leqslant \mu_L, \tag{18}$$

$$\lim_{\rho'\to\rho^*+0} \lim_{V_0\to\infty} \frac{1}{V_0}\frac{\partial}{\partial\rho} \ln f(V_0\rho)\bigg|_{\rho=\rho'} \geqslant \mu_H. \tag{19}$$

To attain the CE, all possible transitions $X_{i,H} \leftrightarrow X_{j,L}$ need to satisfy (i) or (ii). Without such a singularity, the engine cannot attain the CE, as seen in Eq. (8). This is our main result.

Various existing autonomous engines which attain the CE [8,13–27] adopt method (i), where a single particle or a particular value of energy is always transported. In this Rapid Communication, we construct an autonomous engine with the CE which adopts method (ii). In contrast, present autonomous engines which cannot attain the CE [9–12] satisfy neither (i) nor (ii). In the case of the Büttiker-Landauer system, for example, the momentum distributions of the hot bath and the cold bath at the contact point of these two baths are different. Due to this difference, roundtrips of the Brownian particle between two baths cause an energy transport from the hot bath to the cold bath in the form of kinetic energy, which implies finite dissipation.

Concluding remarks. In this Rapid Communication, we derived the necessary condition for autonomous engines to attain the CE. The key property is a special type of singularity as Eqs. (16) and (17), which implies that the same and unique amount of particle number or energy is always transported between two states with different baths. Without such singularities, an autonomous engine never attains the CE. This result is consistent with existing results on the specific models of autonomous engines [5–27].

Such singularities are realized only by the way of transports of (i) a single particle or a particular energy or (ii) a special type of thermodynamic limit. Previous models with the CE adopt method (i), and no concrete model with the CE has adopted method (ii). In this Rapid Communication, we constructed a concrete example of method (ii), and thus it was shown that both methods (i) and (ii) indeed lead to the CE. Here, we should emphasize that method (ii) is different from the following intuitive picture: For the case of a macroscopic heat engine, by decreasing the external force and slowing down the speed of the cyclic process, the engine will reach the CE. In fact, this intuition is wrong for almost all macroscopic engines. Although thermal fluctuation is usually negligible in macroscopic engines, in the case of infinitely slow speed, thermal fluctuation should be taken into account even in macroscopic engines, and the above intuition overlooks this inevitable fluctuation. This fluctuation causes a leakage of particles or energy between two baths. As evidence of this, the inequality (8) still holds for the case of infinitely slow speed.

Our results may give another perspective on the physics of molecular motors. Molecular motors are also autonomous engines, and in most cases they work with a finite chemical potential difference. Our results impose physical restrictions on molecular motors: To attain the CE, chemical heat engines should adopt the method of (i) single particle transports or (ii) thermodynamic limit. These two options appear similar to the two types of molecular motors: working solely (as a kinesin) or collectively (as myosins in a muscle) [35]. It will be interesting if these two characteristics are connected.

Acknowledgments. The author thanks Takahiro Sagawa for fruitful discussions. The author also thanks Eiki Iyoda, Yuki Izumida, Kyogo Kawaguchi, Tomohiko G. Sano, and Akira Shimizu for helpful comments. This work is supported by Grant-in-Aid for JSPS Fellows No. 26-7602.

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