

Thermodynamic Bounds on Efficiency for Systems with Broken Time-Reversal Symmetry

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We show that for systems with broken time-reversal symmetry the maximum efficiency and the efficiency at maximum power are both determined by two parameters: a “figure of merit” and an asymmetry parameter. In contrast to the time-symmetric case, the figure of merit is bounded from above; nevertheless the Carnot efficiency can be reached at lower and lower values of the figure of merit and far from the so-called strong coupling condition as the asymmetry parameter increases. Moreover, the Curzon-Ahlborn limit for efficiency at maximum power can be overcome within linear response. Finally, always within linear response, it is allowed to have Carnot efficiency and nonzero power simultaneously.

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The understanding of the fundamental limits that thermodynamics imposes on the efficiency of thermal machines is a central issue in physics and is becoming more and more practically relevant in the future society. In particular due to the need of providing a sustainable supply of energy and to strong concerns about the environmental impact of the combustion of fossil fuels, there is an increasing pressure to find the best thermoelectric materials [1–4].

A cornerstone result goes back to Carnot [5]. In a cycle between two reservoirs at temperatures T_1 and T_2 ($T_1 > T_2$), the efficiency η , defined as the ratio of the performed work W over the heat Q_1 extracted from the high temperature reservoir, is bounded by the so-called Carnot efficiency η_C :

$$\eta = W/Q_1 \leq \eta_C = 1 - T_2/T_1. \quad (1)$$

The Carnot efficiency is obtained for a quasistatic transformation which requires infinite time and therefore the extracted power, in this limit, reduces to zero. For this reason the notion of efficiency at maximum power has been introduced.

An upper bound for the efficiency at maximum power was proposed long ago by several authors [6–9] and is commonly referred to as the Curzon-Ahlborn upper bound:

$$\eta_{CA} = 1 - \sqrt{T_2/T_1}. \quad (2)$$

The range of validity of this bound has been widely discussed in several interesting papers [10–15]. For the thermoelectric power generation and refrigeration, within linear response and for systems with time-reversal symmetry, both the maximum efficiency and the efficiency at maximum power, are governed by a single parameter, the dimensionless figure of merit

$$ZT = \frac{\sigma S^2}{\kappa} T, \quad (3)$$

where σ is the electric conductivity, S is the thermoelectric power (Seebeck coefficient), κ is the thermal conductivity, and T is the temperature. The maximum efficiency is given by

$$\eta_{\max} = \eta_C \frac{\sqrt{ZT+1} - 1}{\sqrt{ZT+1} + 1}, \quad (4)$$

where η_C is the Carnot efficiency; the efficiency $\eta(\omega_{\max})$ at maximum power ω_{\max} reads [10]

$$\eta(\omega_{\max}) = \eta_{CA}^{(l)} \frac{ZT}{ZT+2}. \quad (5)$$

The only restriction imposed by thermodynamics is $ZT \geq 0$, so that $\eta_{\max} \leq \eta_C$ and $\eta(\omega_{\max}) \leq \eta_{CA}^{(l)}$, where $\eta_{CA}^{(l)} = \eta_C/2$ is the Curzon-Ahlborn efficiency in the linear response regime. The upper bounds η_C and $\eta_{CA}^{(l)}$ are reached when the figure of merit $ZT \rightarrow \infty$. This limit corresponds to the so-called strong coupling condition, for which the Onsager matrix \mathbf{L} becomes singular (that is, $\det \mathbf{L} = 0$) and therefore the ratio J_q/J_p , with J_q heat current and J_p electric (particle) current, is independent of the applied temperature and chemical potential gradients.

In this Letter we investigate, within the linear response regime, the case when time-reversal symmetry is broken, for instance by means of an applied magnetic field [16]. We show that in this case the maximum efficiency as well as the efficiency at maximum power depend on two parameters: the first parameter is a generalization of the figure of merit ZT , while the second, asymmetry parameter, is the ratio of the off-diagonal terms of the Onsager matrix. The presence of a second parameter is highly important since it

offers an additional freedom in the design of high-performance thermoelectric devices. In particular it turns out that the figure of merit is bounded from above when the asymmetry parameter is different from unity; nevertheless the Carnot efficiency is reached at lower and lower values of the figure of merit and far from the strong coupling condition as the asymmetry parameter increases. Furthermore, the Curzon-Ahlborn limit can be overcome. Finally, within linear response it is not forbidden to have Carnot efficiency and nonzero power simultaneously.

The model we consider is sketched in Fig. 1. Both electric and heat currents flow along the horizontal axis. The system is in contact with left and right reservoirs at temperatures T_L and T_R and chemical potentials μ_L and μ_R . Even though fluxes are one dimensional, the motion inside the system can be two or three dimensional. We start from the equations connecting fluxes and thermodynamic forces within linear irreversible thermodynamics [17]:

$$\begin{aligned} J_\rho(\mathbf{B}) &= L_{\rho\rho}(\mathbf{B})X_1 + L_{\rho q}(\mathbf{B})X_2, \\ J_q(\mathbf{B}) &= L_{q\rho}(\mathbf{B})X_1 + L_{qq}(\mathbf{B})X_2, \end{aligned} \quad (6)$$

where J_ρ and J_q are the particle and heat currents, \mathbf{B} an applied magnetic field or any parameter breaking time reversibility (such as the Coriolis force, etc.), and $X_1 = -\beta\Delta\mu$, $X_2 = \Delta\beta = -\Delta T/T^2$ the thermodynamic forces, with $\Delta\mu = \mu_R - \mu_L$, $\beta = 1/T$, $\Delta\beta = \beta_R - \beta_L$. $\Delta T = T_R - T_L$ is assumed to be small compared to $T_L \approx T_R \approx T$. Without loss of generality we assume $T_L > T_R$. Therefore, the parameter X_2 is always positive, while the sign of X_1 is determined in such a way that the work done by the particle current is positive. Note that the sign of the current is taken positive if it flows from the left to the right reservoir.

The positivity of the entropy production rate,

$$\dot{S} = J_\rho X_1 + J_q X_2 \geq 0, \quad (7)$$

implies for the Onsager coefficients L_{ij} ($i, j = \rho, q$) that

$$\begin{aligned} L_{\rho\rho}(\mathbf{B}) &\geq 0, & L_{qq}(\mathbf{B}) &\geq 0, \\ L_{\rho\rho}(\mathbf{B})L_{qq}(\mathbf{B}) - \frac{1}{4}[L_{\rho q}(\mathbf{B}) + L_{q\rho}(\mathbf{B})]^2 &\geq 0. \end{aligned} \quad (8)$$

Moreover, the Onsager-Casimir relations in the presence of a magnetic field read

$$L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B}). \quad (9)$$

The Onsager coefficients are related to the familiar transport coefficients σ , κ , S as follows [17]:

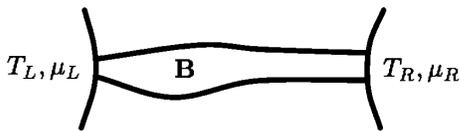


FIG. 1. Schematic drawing of the model.

$$\sigma(\mathbf{B}) = \frac{e^2}{T} L_{\rho\rho}(\mathbf{B}), \quad (10)$$

$$\kappa(\mathbf{B}) = \frac{1}{T^2} \frac{\det \mathbf{L}(\mathbf{B})}{L_{\rho\rho}(\mathbf{B})}, \quad (11)$$

$$S(\mathbf{B}) = \frac{L_{\rho q}(\mathbf{B})}{eTL_{\rho\rho}(\mathbf{B})}, \quad S(-\mathbf{B}) = \frac{L_{q\rho}(\mathbf{B})}{eTL_{\rho\rho}(\mathbf{B})}, \quad (12)$$

where e is the electron charge and \mathbf{L} denotes the Onsager matrix with matrix elements L_{ij} . Note that the Onsager-Casimir relations $L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B})$ imply $\sigma(\mathbf{B}) = \sigma(-\mathbf{B})$ and $\kappa(\mathbf{B}) = \kappa(-\mathbf{B})$, while *a priori* it is possible to have $S(\mathbf{B}) \neq S(-\mathbf{B})$. In what follows, to improve readability we do not write \mathbf{B} explicitly as an argument in the Onsager coefficients, unless necessary.

Efficiency at maximum power.— The efficiency η , under steady-state conditions, is given by the ratio of the output power over the heat current (leaving the hot reservoir):

$$\eta = \frac{\omega}{J_q}. \quad (13)$$

The output power

$$\omega = J_\rho \Delta\mu = -J_\rho T X_1 \quad (14)$$

is maximal when

$$X_1 = -\frac{L_{\rho q}}{2L_{\rho\rho}} X_2 \quad (15)$$

and is given by

$$\omega_{\max} = \frac{T}{4} \frac{L_{\rho q}^2}{L_{\rho\rho}} X_2^2 = \frac{\eta_C}{4} \frac{L_{\rho q}^2}{L_{\rho\rho}} X_2, \quad (16)$$

where $\eta_C = -\Delta T/T = T X_2$ is the Carnot efficiency.

The efficiency at maximum power

$$\eta(\omega_{\max}) = \frac{\omega_{\max}}{J_q} = \eta_{\text{CA}}^{(l)} \frac{1}{2 \frac{L_{\rho\rho}L_{qq}}{L_{\rho q}^2} - \frac{L_{q\rho}}{L_{\rho q}}} \quad (17)$$

is seen to depend on two parameters:

$$x \equiv \frac{L_{\rho q}}{L_{q\rho}} = \frac{S(\mathbf{B})}{S(-\mathbf{B})}, \quad (18)$$

$$y \equiv \frac{L_{\rho q}L_{q\rho}}{\det \mathbf{L}} = \frac{\sigma(\mathbf{B})S(\mathbf{B})S(-\mathbf{B})}{\kappa(\mathbf{B})} T \quad (19)$$

and writes

$$\eta(\omega_{\max}) = \eta_{\text{CA}}^{(l)} \frac{xy}{2+y}. \quad (20)$$

In the particular case $x = 1$, y reduces to the $ZT = (\sigma S^2/k)T$ figure of merit of the time-symmetric case and Eq. (20) reduces to Eq. (5). While thermodynamics does not impose any restriction on the attainable values of the asymmetry parameter x , the third inequality in (8) implies

$$\begin{aligned} h(x) &\leq y \leq 0 & \text{if } x < 0, \\ 0 &\leq y \leq h(x) & \text{if } x > 0, \end{aligned} \quad (21)$$

where $h(x) = 4x/(x-1)^2$ and we have taken into account that x and y must have the same sign since (8) implies $\det \mathbf{L} \geq 0$ and $y = xL_{qp}^2/\det \mathbf{L}$. The function $h(x)$ is drawn in Fig. 2. Note that $\lim_{x \rightarrow 1} h(x) = \infty$ and therefore there is no upper bound on $y(x=1) = ZT$. It is easy to check that the maximum η^* in (20) is achieved for $y = h(x)$, that is,

$$\eta(\omega_{\max}) \leq \eta^* = \eta_C \frac{x^2}{x^2 + 1}. \quad (22)$$

The function $\eta^*(x)$ is drawn in Fig. 3 (dashed curve). Several remarks are in order. To begin with, in the absence of the magnetic field ($x = 1$) $L_{\rho q} = L_{q\rho}$ and the Curzon-Ahlborn limit for the linear response regime is recovered: $\eta^*(x=1) = \eta_{CA}^{(l)} = \eta_C/2$. Furthermore, the Curzon-Ahlborn limit can be overcome when $|x| > 1$ and η^* approaches the Carnot efficiency when $|x| \rightarrow \infty$. We also note that if the magnetic field \mathbf{B} is reversed, owing to the Onsager-Casimir relations, x is replaced by $1/x$. From inequality (22) it then follows that the average efficiency for \mathbf{B} and $-\mathbf{B}$ cannot overcome the Curzon-Ahlborn limit: $\frac{1}{2}(\eta^*(x) + \eta^*(1/x)) \leq \eta_{CA}^{(l)}$.

Maximum efficiency.— The maximum of

$$\eta = \frac{\Delta\mu J_\rho}{J_q} = \frac{-TX_1(L_{\rho\rho}X_1 + L_{\rho q}X_2)}{L_{qq}X_1 + L_{qq}X_2} \quad (23)$$

over X_1 , for fixed X_2 and under the condition $J_q > 0$, is achieved for

$$X_1 = \frac{L_{qq}}{L_{q\rho}} \left(-1 + \sqrt{\frac{\det \mathbf{L}}{L_{\rho\rho}L_{qq}}} \right) X_2 \quad (24)$$

and is given by

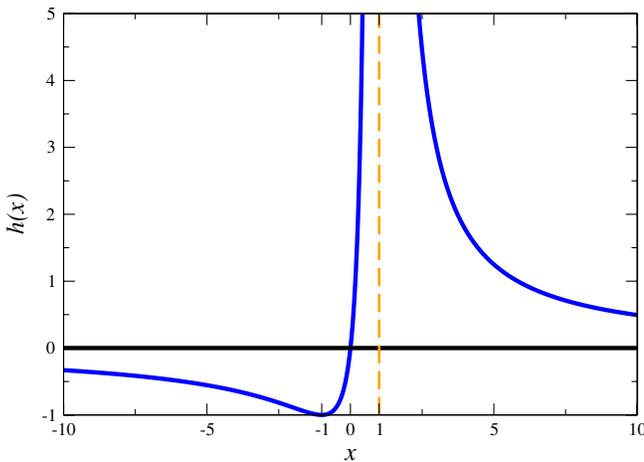


FIG. 2 (color online). Function $h(x)$ (blue solid curve). This function has a vertical asymptote at $x = 1$ (dashed line). Thermodynamics restricts the parameter y between $y = 0$ and $y = h$.

$$\eta_{\max} = \eta_C x \frac{\sqrt{y+1} - 1}{\sqrt{y+1} + 1}. \quad (25)$$

Note that (21) implies $y \geq -1$ for any x , so that η_{\max} is as expected a real-valued function. We point out that at $x = 1$ we recover the well-known efficiency expression (4). For a given asymmetry parameter x the maximum η_M of (25) is again reached when $y = h(x)$. By substituting the function $h(x)$ into Eq. (25) we find

$$\eta_M = \begin{cases} \eta_C x^2 & \text{if } |x| \leq 1, \\ \eta_C & \text{if } |x| \geq 1. \end{cases} \quad (26)$$

The function $\eta_M(x)$ is drawn in Fig. 3 (full curve). On the other hand, when $x \neq 1$ the figure of merit y alone is no longer sufficient to determine the thermoelectric efficiency: η_{\max} depends on both x and y . Moreover, the Carnot limit can be achieved only when $|x| \geq 1$ [18]. We point out that when $|x| \rightarrow \infty$, the figure of merit y required to get the Carnot efficiency becomes increasingly smaller. When $|x| \geq 1$ the Carnot efficiency is obtained under the condition $y = h(x)$, which implies $\det \mathbf{L} = (L_{\rho q} - L_{q\rho})^2/4$. Therefore Carnot efficiency and $L_{\rho q} \neq L_{q\rho}$ imply $\det \mathbf{L} > 0$, that is, the strong coupling condition is not fulfilled.

The entropy production rate at maximum efficiency is

$$\dot{S}(\eta_M) = \begin{cases} \frac{(L_{\rho q}^2 - L_{q\rho}^2)^2}{4L_{\rho\rho}L_{qq}^2} X_2^2 & \text{if } |x| < 1, \\ 0 & \text{if } |x| \geq 1. \end{cases} \quad (27)$$

Hence there is no entropy production at $|x| \geq 1$, in agreement with the fact that in this regime $\eta_M = \eta_C$.

We can now derive the output power at maximum efficiency:

$$\omega(\eta_M) = \frac{\eta_M}{4} \frac{|L_{\rho q}^2 - L_{q\rho}^2|}{L_{\rho\rho}} X_2. \quad (28)$$

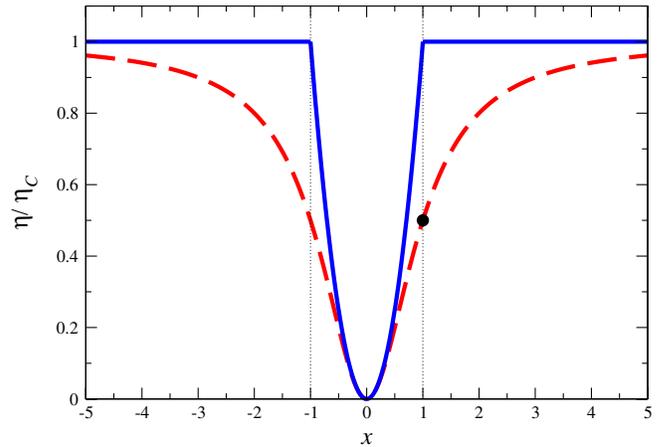


FIG. 3 (color online). Ratio η/η_C as a function of the asymmetry parameter x , with $\eta = \eta^*$ (dashed curve) and $\eta = \eta_M$ (solid curve). The black filled circle corresponds to the Curzon-Ahlborn limit at $x = 1$: $\eta_{CA}^{(l)} = \eta_C/2$.

From relation (13), the heat current is determined as $J_q = |L_{\rho q}^2 - L_{qq}^2|X_2/(4L_{\rho\rho})$. It is readily seen from (16) and (28) that $\omega(\eta_M) \leq \omega_{\max}$. It is important to note that $\omega(\eta_M) \rightarrow \omega_{\max}$ when $|x| \rightarrow \infty$, as expected since in this limit $\eta^* \rightarrow \eta_M = \eta_C$. Therefore, in this limit we have Carnot efficiency and power ω_{\max} simultaneously.

In summary, we have shown that when time-reversal symmetry is broken both the maximum efficiency and the efficiency at maximum power are no longer exclusively determined by the figure of merit ZT . Two parameters are needed, an asymmetry parameter x and a parameter y which reduces to ZT in the symmetric limit $x = 1$. In the case $|x| > 1$, it is possible to overcome the Curzon-Ahlborn limit within linear response and to reach the Carnot efficiency, for an increasingly smaller and smaller figure of merit y as $|x|$ becomes larger. With regard to the practical relevance of the results presented here, we should note that in the noninteracting case $S(\mathbf{B}) = S(-\mathbf{B})$, thus implying $x = 1$, is a consequence of the symmetry properties of the scattering matrix [19]. On the other hand, the Onsager-Casimir symmetry relations do not impose the symmetry of the Seebeck coefficient under the exchange $\mathbf{B} \rightarrow -\mathbf{B}$. Therefore, this symmetry may be violated when electron-phonon and electron-electron interactions are taken into account. While the Seebeck coefficient has always been found to be an even function of the magnetic field in two-terminal purely metallic mesoscopic systems [20], Andreev interferometer experiments [21] and recent theoretical studies [22,23] have shown that systems in contact with a superconductor or with a heat bath can exhibit nonsymmetric thermopowers. It is a challenging problem to find realistic setups with x significantly different from unity, while approaching the Carnot efficiency.

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 [18] It is interesting that, in the case of a refrigerator, the maximum efficiency $\eta^{(r)} = J_q/\omega$ ($J_q < 0$, $\omega < 0$), achieved for

$$X_1 = \frac{L_{qq}}{L_{q\rho}} \left(-1 - \sqrt{\frac{\det \mathbf{L}}{L_{\rho\rho} L_{qq}}} \right) X_2, \quad (29)$$

is given by

$$\eta_{\max}^{(r)} = \eta_C \frac{1}{x} \frac{\sqrt{y+1} - 1}{\sqrt{y+1} + 1}. \quad (30)$$

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