Thermodynamic Bound on Heat-to-Power Conversion

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In systems described by the scattering theory, there is an upper bound, lower than Carnot, on the efficiency of steady-state heat-to-work conversion at a given output power. We show that interacting systems can overcome such bound and saturate, in the thermodynamic limit, the much more favorable linear-response bound. This result is rooted in the possibility for interacting systems to achieve the Carnot efficiency at the thermodynamic limit without delta-energy filtering, so that large efficiencies can be obtained without greatly reducing power.

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Introduction.—The increasing energy demand and the depletion and environmental impact of fossil fuels calls for renewable and eco-friendly energy resources. In this frame, nanoscale thermal engines [1–12] will play an important role and might become part of the energetic mix of the future. A crucial point is the efficiency of such engines. Given any heat engine operating between two reservoirs at temperature T_L and T_R ($T_L > T_R$), the efficiency of energy conversion is upper bounded by the Carnot efficiency $\eta_C = 1 - T_R/T_L$. This limit can be achieved for dissipationless heat engines. Such ideal machines operate reversibly and infinitely slowly, and therefore the extracted power vanishes in the Carnot limit. For any practical purpose it is therefore crucial to consider the *power-efficiency trade-off*, in order to design devices that work at the maximum possible efficiency for a given output power.

For steady-state conversion of heat to work in quantum systems which can be modeled by the Landauer-Büttiker scattering theory, this problem was solved theoretically by Whitney [13,14]. Indeed, he found a bound on the efficiency at a given output power P, which equals the Carnot efficiency at $P = 0$, and decays with increasing P. This upper bound is achieved when only particles within a given energy window (determined by the desired output power P) of width $\delta(P)$ can be transmitted through the system. The Carnot efficiency is obtained for delta-energy filtering [15–17], that is, when $\delta \to 0$, and in such limit the output power vanishes. This interesting result establishes a bound for an important class of systems. Now the relevant question is, how general is this bound? For general interacting systems, can this bound be overcome, thus allowing for a better power-efficiency trade-off?

In this Letter, we give a positive answer to this question for classical systems. Indeed, we show that interacting, nonintegrable momentum-conserving systems overcome the bound from the scattering theory. These systems can achieve the Carnot efficiency at the thermodynamic limit, with a much more favorable power-efficiency trade-off than allowed by the scattering theory. Therefore, interactions can significantly improve the performance of steady-state heat-to-work conversion. This result is rooted in the possibility, for interacting systems, to achieve the Carnot efficiency without delta-energy filtering. Our results are illustrated by means of extensive numerical simulations of classical models of elastically colliding particles.

Classical reservoirs.—For concreteness, we consider a one-dimensional system (even though, as discussed in the Conclusions and shown in Sec. D of the Supplemental Material [18], our analysis can be extended to higher dimensions), whose ends are in contact with left and right reservoirs, characterized by temperature T_α and electrochemical potential μ_α ($\alpha = L, R$). The reservoirs are modeled as infinite one-dimensional ideal gases, with particle velocities described by the Maxwell-Boltzmann distribution, $F_\alpha(v) = \sqrt{m/(2\pi k_B T_\alpha)}\exp[-mv^2/(2k_B T_\alpha)]$, where k_B is the Boltzmann constant and m the mass of the particles. We use a stochastic model of the reservoirs [19,20]: whenever a particle of the system crosses the boundary which separates the system from the left or right reservoir, it is removed. On the other hand, particles are injected into the system from the boundaries, with rates γ_α. The injection rate γ_α is computed by counting how many particles from reservoir α cross the reservoir-system boundary per unit time: $\gamma_\alpha = \rho_\alpha \int_0^\infty dv v F_\alpha(v) = \rho_\alpha \sqrt{k_B T_\alpha/(2\pi m)}$, with ρ_α the particle number density of the ideal gas in reservoir α. A standard derivation [21] then shows that the density ρ_α is related to the electrochemical potential μ_α as follows: $\mu_\alpha = k_B T_\alpha \ln(\rho_\alpha \lambda_\alpha)$, where $\lambda_\alpha = h/\sqrt{2\pi m k_B T_\alpha}$ is the de Broglie thermal wavelength and h the Planck constant.

Noninteracting systems.—In this case, the particle current reads [21]

$$J_\rho = \gamma_L \int_0^\infty d\epsilon u_L(\epsilon)\mathcal{T}(\epsilon) - \gamma_R \int_0^\infty d\epsilon u_R(\epsilon)\mathcal{T}(\epsilon), \qquad (1)$$

where $u_\alpha(\epsilon) = \beta_\alpha e^{-\beta_\alpha \epsilon}$, with $\beta_\alpha = (k_B T_\alpha)^{-1}$, is the energy distribution of the particles injected from reservoir α and $\mathcal{T}(\epsilon)$ is the transmission probability for a particle with energy ϵ to transit from one end to another of the system, $0 \le \mathcal{T}(\epsilon) \le 1$. We can equivalently rewrite the particle current in a form which can be seen as the classical analogue to the Landauer-Büttiker approach:

$$J_\rho = \frac{1}{h}\int_0^\infty d\epsilon [f_L(\epsilon) - f_R(\epsilon)]\mathcal{T}(\epsilon), \qquad (2)$$

where $f_\alpha(\epsilon) = e^{-\beta_\alpha(\epsilon - \mu_\alpha)}$ is the Maxwell-Boltzmann distribution function. Similarly, we obtain the heat current from reservoir α as

$$J_{h,\alpha} = \frac{1}{h}\int_0^\infty d\epsilon (\epsilon - \mu_\alpha)[f_L(\epsilon) - f_R(\epsilon)]\mathcal{T}(\epsilon). \qquad (3)$$

To proceed we take the reference electrochemical potential to be that of reservoir L and set $\mu_L = 0$. Following the same steps as done in Refs. [13,14] for the quantum case, we find the transmission function that maximizes the efficiency of the heat engine, $\eta(P) = P/J_{h,L}$, for a given output power $P = (\Delta\mu)J_\rho$, with $\Delta\mu = \mu_R - \mu_L > 0$ and $P, J_{h,L} > 0$. It turns out that the optimal $\mathcal{T}$ is a boxcar function, $\mathcal{T}(\epsilon) = 1$ for $\epsilon_0 < \epsilon < \epsilon_1$ and $\mathcal{T}(\epsilon) = 0$ otherwise. Here $\epsilon_0 = \Delta\mu/\eta_C$ is obtained from the condition $f_L(\epsilon_0) = f_R(\epsilon_0)$ and ϵ_1 can be determined numerically by solving the equation $\epsilon_1 = \Delta\mu J'_{h,L}/P'$, where the prime indicates the derivative over $\Delta\mu$ for fixed $\mathcal{T}$ (this equation is transcendental since $J_{h,L}$ and P depend on ϵ_1). The maximum achievable power (according to scattering theory) is obtained when $\epsilon_1 \to \infty$:

$$P_{\max}^{(\mathrm{st})} = A\frac{\pi^2}{h}k_B^2(\Delta T)^2, \qquad (4)$$

where $\Delta T = T_L - T_R$ and $A \approx 0.0373$. Note that $\Delta\mu$ is determined from the above optimization procedure; in particular, at $P_{\max}^{(\mathrm{st})}$ we obtain $\Delta\mu = k_B \Delta T$. At small output power, $P/P_{\max}^{(\mathrm{st})} \ll 1$, the upper bound on efficiency approaches the Carnot efficiency as follows:

$$\eta(P) \le \eta_{\max}^{(\mathrm{st})}(P) = \eta_C\left(1 - B\sqrt{\frac{T_R}{T_L}\frac{P}{P_{\max}^{(\mathrm{st})}}}\right), \qquad (5)$$

where $B \approx 0.493$. In the limit $\epsilon_1 \to \epsilon_0$, $P \to 0$ and $\eta \to \eta_C$. In this case, we recover the well-known delta-energy filtering mechanism to achieve the Carnot efficiency [15–17]. Namely, we recover the Carnot limit when transmission is possible only inside an energy window of width $\delta = \epsilon_1 - \epsilon_0 \to 0$. It is intuitive that selecting transmission over a tiny energy window greatly reduces power production. It is therefore natural to expect that a different mechanism to reach Carnot efficiency might allow a larger power production. Indeed, in what follows we show that for interacting, momentum-conserving systems, where the Carnot efficiency can be reached without delta-energy filtering (see Sec. C in the Supplemental Material [18]), a greatly improved power-efficiency trade-off can be obtained.

Momentum-conserving systems.—We consider a system of elastically colliding particles, in contact with two reservoirs tuned at different temperatures and electrochemical potentials in order to maintain a steady flow of particles and heat. The equations connecting fluxes and thermodynamic forces within linear response (an approximation that we will show later to be valid for our model) are [22,23]

$$\begin{pmatrix} J_\rho \\ J_u \end{pmatrix} = \begin{pmatrix} L_{\rho\rho} & L_{\rho u} \\ L_{u\rho} & L_{uu} \end{pmatrix}\begin{pmatrix} -\nabla(\beta\mu) \\ \nabla\beta \end{pmatrix}, \qquad (6)$$

where J_ρ is the steady particle current, J_u is the steady energy current, and L_{ij} (with $i, j = \rho, u$) are the kinetic (Onsager) coefficients. Hereafter we will discuss our results in the language of thermoelectricity, even though they could equally well refer to other steady-state heat-to-work conversion phenomena like thermodiffusion. The Onsager coefficients are then related to the familiar transport coefficients as follows:

$$\sigma = \frac{e^2}{T}L_{\rho\rho}, \quad \kappa = \frac{1}{T^2}\frac{\det\mathbb{L}}{L_{\rho\rho}}, \quad S = \frac{1}{eT}\left(\frac{L_{\rho u}}{L_{\rho\rho}} - \mu\right). \qquad (7)$$

Here σ is the electrical conductivity, κ is the thermal conductivity, and S is the thermopower. Additionally, e is the charge of the conducting particles, $T \approx T_L \approx T_R$ and $\mu \approx \mu_L \approx \mu_R$ in the linear response formulas, and $\det\mathbb{L}$ denotes the determinant of the (Onsager) matrix of kinetic coefficients. Thermodynamics imposes $\det\mathbb{L} \ge 0$, $L_{\rho\rho} \ge 0$, $L_{uu} \ge 0$, and the Onsager reciprocity relations ensure (for systems with time-reversal symmetry) that $L_{u\rho} = L_{\rho u}$. The maximum efficiency for energy conversion achievable by the system is a monotonically growing function of the thermoelectric figure of merit ZT [12]:

$$ZT = \frac{\sigma S^2}{\kappa} T = \frac{(L_{u\rho} - \mu L_{\rho\rho})^2}{\det \mathbb{L}}. \quad (8)$$

Thermodynamics imposes $ZT \geq 0$, with the efficiency $\eta = 0$ when $ZT = 0$ and $\eta \to \eta_C$ when $ZT \to \infty$.

Hereafter, we illustrate the breaking of bound Eq. (5) by considering a one-dimensional, diatomic chain of hard-point elastically colliding particles connected to reservoirs, with masses $m_i \in \{m, M\}$ and $m \neq M$. (See Ref. [21] for details of the model.) We have performed a nonequilibrium calculation of the transport coefficients and then of the figure of merit ZT (we have developed a method to determine very accurately the transport coefficients; see the Supplemental Material, Sec. B, for details [18]). In our simulations, we set $k_B = m = e = 1$ and the system length L to be equal to the mean number of particles N inside the system. Our data shown in Fig. 1 as well as theoretical arguments [24] show that the electrical conductivity $\sigma \propto N$, the thermal conductivity $\kappa \propto N^{\xi}$, with the power $\xi = 1/3$ predicted by hydrodynamics approach [25,26], the thermopower is asymptotically size independent, and therefore $ZT \propto N^{1-\xi} = N^{2/3}$.

In Fig. 2, we show, for a given ΔT and different system sizes, the relative efficiency η/η_C as a function of the normalized power $P/P_{\max}$. Note that these curves have two branches as they are obtained by changing $\Delta\mu$ from zero (where $P = 0$) up to the stopping value, where again $P = 0$, since the electrochemical potential difference becomes too high to be overcome by the temperature difference. In between, power first increases, up to $P = P_{\max}$, and then decreases, leading to a two-branch curve. In the same figure, we also show the analytical result from linear response [12]:

$$\frac{\eta}{\eta_C} = \frac{\frac{P}{P_{\max}}}{2\left(1 + \frac{2}{ZT} \mp \sqrt{1 - \frac{P}{P_{\max}}}\right)}, \quad (9)$$

where the figure of merit ZT and $P_{\max} = S^2\sigma(\Delta T)^2/(4N)$, derived from Eqs. (6) and (7), have been computed previously (see Fig. 1). In spite of the not so small value of $\Delta T/T = 0.2$, there is a good agreement between the results of our numerical simulations and the universal linear response behavior given by Eq. (9). Moreover, such agreement improves with increasing the system size, as expected since $|\nabla T| = \Delta T/N$ decreases when N increases. For any given ΔT, we expect the linear response to correctly describe the transport properties of our model for large enough system sizes. In Fig. 2, we also show the parabolic curve corresponding to Eq. (9) for $ZT = \infty$ (obtained in our model in the thermodynamic limit $N \to \infty$), whose upper branch is the universal linear response upper bound to efficiency for a given power P. The expansion of such a curve for $P/P_{\max} \ll 1$ leads to

$$\eta(P) \leq \eta_{\mathrm{lr}}(P) = \eta_C\left(1 - \frac{1}{4}\frac{P}{P_{\max}}\right), \quad (10)$$

which sets a much less restrictive bound for efficiency-power trade-off than the bound Eq. (5) obtained above for noninteracting systems. Our above reported numerical results strongly suggest that the linear-response bound is saturated by our model in the *thermodynamic limit*.

To illustrate the breaking of bound Eq. (5) for *finite* system sizes, we compute the maximum efficiency $\eta_{\max}$ and the corresponding power $P(\eta_{\max})$, for different system

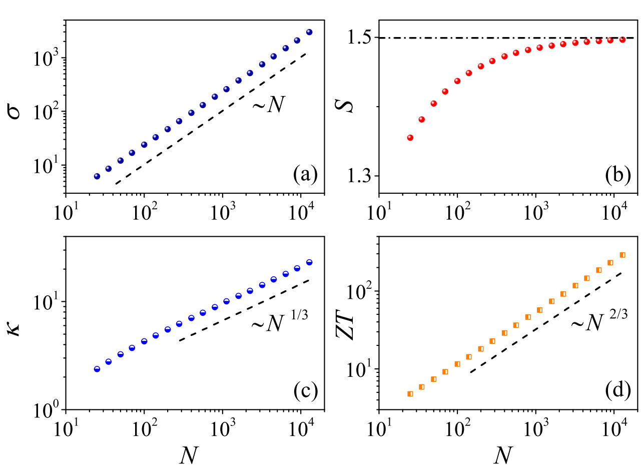

FIG. 1. Electrical conductivity σ (a), thermopower S (b), thermal conductivity κ (c), and figure of merit ZT (d) as a function of the mean number N of particles inside the system, for the one-dimensional, diatomic hard-point gas. Here and in the other figures, the data are obtained for $M = 3$, $T = 1$, and $\mu = 0$.

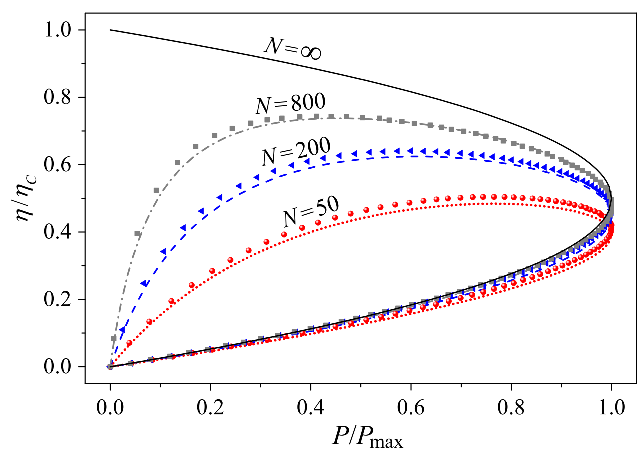

FIG. 2. Relative efficiency η/η_C versus normalized power $P/P_{\max}$ for $\Delta T = 0.2$ ($T_L = 1.1$, $T_R = 0.9$) and different system sizes. The dotted, dashed, and dot-dashed curves show the expectation from linear response, Eq. (9), at the $ZT(N)$ value corresponding to the given system size N. The solid line is Eq. (9) for $ZT = \infty$, corresponding to $N = \infty$ in our model. The upper branch of this curve sets the linear-response upper bound on efficiency for a given power.

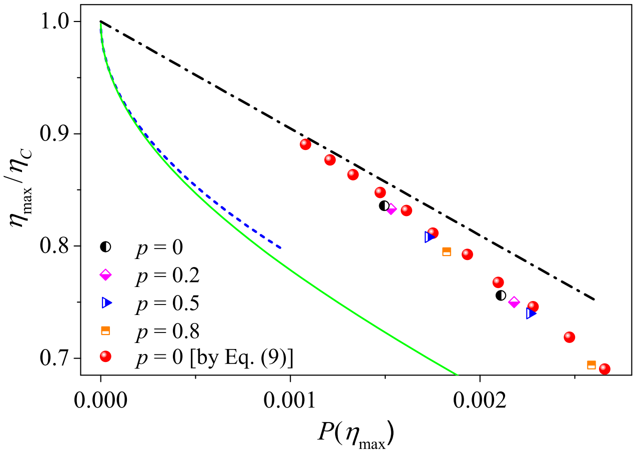

FIG. 3. Maximum efficiency η_{max} versus the corresponding power $P(\eta_{max})$, from linear response with the values of ZT obtained numerically (red circles) and directly from numerical computation of power and efficiency (black and white circles) for various system sizes with $T_L = 1.1$ and $T_R = 0.9$. The dot-dashed line is for the analytical expectation from linear response at large ZT, Eq. (11). We also show the bound for classical noninteracting systems (solid line) and its approximation at the low power limit given by Eq. (5) (dashed line) as a comparison. Data from the stochastic model described in the text, with p crossing probability each time two particles meet, are also reported (for further details on this model, see Sec. A in the Supplemental Material [18]).

sizes. The obtained results, shown as black and white circles in Fig. 3, are in agreement with the linear response predictions, obtained from Eq. (9) at different values of ZT (red circles). For $ZT \to \infty$ (obtained when $N \to \infty$), $\eta_{max} \to \eta_C$ and $P(\eta_{max}) \to 0$. In the limit of large ZT, from Eq. (9) we obtain

$$\eta_{max} = \eta_C \left(1 - \frac{1}{2}\frac{P(\eta_{max})}{P_{max}}\right). \tag{11}$$

This power-efficiency trade-off when approaching the Carnot efficiency is much more favorable than the bound for noninteracting systems, also shown for comparison in Fig. 3. To investigate the dependence of power and efficiency on the interaction strength, we introduce a parameter p as follows: When two particles meet, they pass through each other with probability p, while they collide elastically with probability $1 - p$. For our original hard-point model, $p = 0$, while for the noninteracting case, $p = 1$. We can see in Fig. 3 that data at different values of p stay on a single curve, as expected from linear response. While for a given system size by decreasing interactions (i.e., by increasing p) we reduce ZT and therefore deteriorate the performance of energy conversion, ZT still grows with the system size. In short, the larger p, the larger the system size is required to have a given number of collisions per particle crossing the system. Only in the noninteracting case we obtain $ZT = 1$ ($\eta/\eta_C \approx 0.17$) for all system sizes [24].

Conclusions and discussion.—In this Letter, we have shown that classical interacting systems allow, for a given power, a much higher efficiency than the one achievable in the noninteracting case. This result shows that interactions can significantly improve the performance of heat-to-work conversion. Our results are based on the fact that for momentum-conserving systems the Carnot efficiency can be achieved at the thermodynamic limit without delta-energy filtering. While we have considered for illustrative purposes a one-dimensional, diatomic disordered chain of hard-point elastically colliding particles, our theoretical considerations can be as well extended to other momentum-conserving systems, also of higher dimensions [27,28]. In the noninteracting case, for d-dimensional systems connected to reservoirs via openings of linear size l_α, the injection rate of particles from reservoir α to the system is proportional to $(l_\alpha/\lambda_\alpha)^{d-1}$, and therefore the maximum power scales linearly with this quantity, which plays the role of the number of transverse modes in a classical context. The corresponding noninteracting bound on efficiency at a given power is broken by momentum-conserving systems, as shown in the Supplemental Material, Sec. D [18], for the two-dimensional multiparticle collision model [29]. Finally, we have also considered refrigeration (see again the Supplemental Material, Sec. E [18]) and shown that, thanks to interactions, one can greatly exceed the bound on efficiency for a given cooling power which applies to systems described by the scattering theory. While we conjecture that our results also apply in the quantum case for systems with momentum conservation, such extension remains as a challenging task for future investigations.

Besides their fundamental interest, our findings for momentum-conserving systems could be of practical relevance in situations where the elastic mean free path of the conducting particles is much longer than the length scale over which interactions are effective in exchanging momenta between the particles, as it might happen in high-mobility two-dimensional electron gases at low temperatures. Moreover, our results might find applications in the context of cold atoms, where a thermoelectric heat engine has already been demonstrated for weakly interacting particles [30]. More recent experimental results on coupled particle and heat transport through a quantum point contact connecting two reservoirs of interacting Fermi gases have shown a strong violation of the Wiedemann-Franz law which could not be explained by the Landauer-Büttiker scattering theory [31]. It can be envisaged that in such systems, which can be considered as thermoelectric devices with high efficiency [31], the noninteracting bound on efficiency for a given (cooling) power could be outperformed, with possible applications to the refrigeration of atomic gases.

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