Thermopower and thermoelectric efficiency in systems with broken time-reversal symmetry

Giuliano Benenti

Center for Nonlinear and Complex Systems
Univ. Insubria, Como, Italy

In collaboration with:
Keiji Saito (Yokohama),
Giulio Casati, Vinitha Balachandran (Como),
Tomaz Prosen, Martin Horvat (Ljubljana)

OUTLINE

For systems with time-reversal symmetry Carnot efficiency is achieved if and only if we are in the strong coupling regime (singular Onsager matrix):

$$J_q \propto J_\rho$$

And when a magnetic field is applied to the system?

Thermoelectric efficiency in systems with time-reversal breaking

Asymmetric thermopower?

For systems with time-reversal symmetry and within **linear response**

FIGURE OF MERIT

$$ZT = \frac{L_{q\rho}^2}{\det \mathbf{L}} = \frac{\sigma S^2}{k} T$$

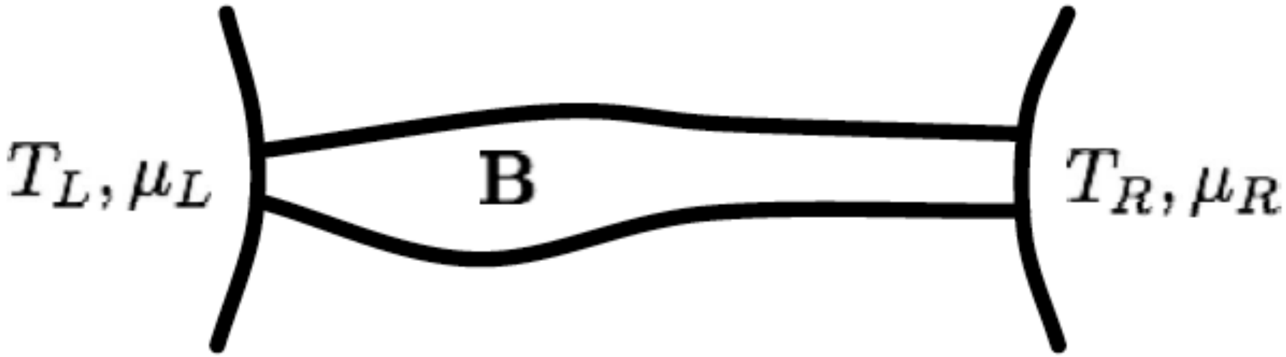
MAXIMUM EFFICIENCY

$$\eta_C \, \frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+1}$$

EFFICIENCY AT MAXIMUM POWER

$$\eta(\omega_{\max}) = \frac{\eta_C}{2} \, \frac{ZT}{ZT+2}$$

And when time-reversal is broken?



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

$$X_1 = -\beta \Delta\mu$$

$$X_2 = \Delta\beta = -\Delta T / T^2$$

$$\beta = 1/T$$

$$\Delta\mu = \mu_R - \mu_L$$

$$\Delta\beta = \beta_R - \beta_L$$

$$\Delta T = T_R - T_L$$

B applied magnetic field or any parameter breaking time-reversibility such as the Coriolis force, etc.

we assume $T_L > T_R$

Constraints from thermodynamics

POSITIVITY OF THE ENTROPY PRODUCTION:

$$\dot{S} = J_\rho X_1 + J_q X_2 \geq 0 \quad \Rightarrow \quad \begin{cases} L_{\rho\rho} \geq 0, \\ L_{qq} \geq 0, \\ L_{\rho\rho} L_{qq} - \frac{1}{4}(L_{\rho q} + L_{q\rho})^2 \geq 0 \end{cases}$$

ONSAGER-CASIMIR RELATIONS:

$$L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B}) \quad \Rightarrow \quad \begin{aligned} \sigma(\mathbf{B}) &= \sigma(-\mathbf{B}) \\ \kappa(\mathbf{B}) &= \kappa(-\mathbf{B}) \end{aligned}$$

in general, $S(\mathbf{B}) \neq S(-\mathbf{B})$

EFFICIENCY AT MAXIMUM POWER

Output power $\omega = J_\rho \Delta\mu = -J_\rho T X_1$

maximum when $X_1 = -\dfrac{L_{\rho q}}{2L_{\rho\rho}} X_2$

$$\omega_{\max} = \frac{T}{4}\frac{L_{\rho q}^2}{L_{\rho\rho}} X_2^2 = \frac{\eta_C}{4}\frac{L_{\rho q}^2}{L_{\rho\rho}} X_2$$

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

$$\eta(\omega_{\max}) = \frac{\omega_{\max}}{J_q} = \frac{\eta_C}{2}\frac{1}{2\frac{L_{\rho\rho}L_{qq}}{L_{\rho q}^2} - \frac{L_{q\rho}}{L_{\rho q}}}$$

Efficiency at maximum power depends on two parameters

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

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

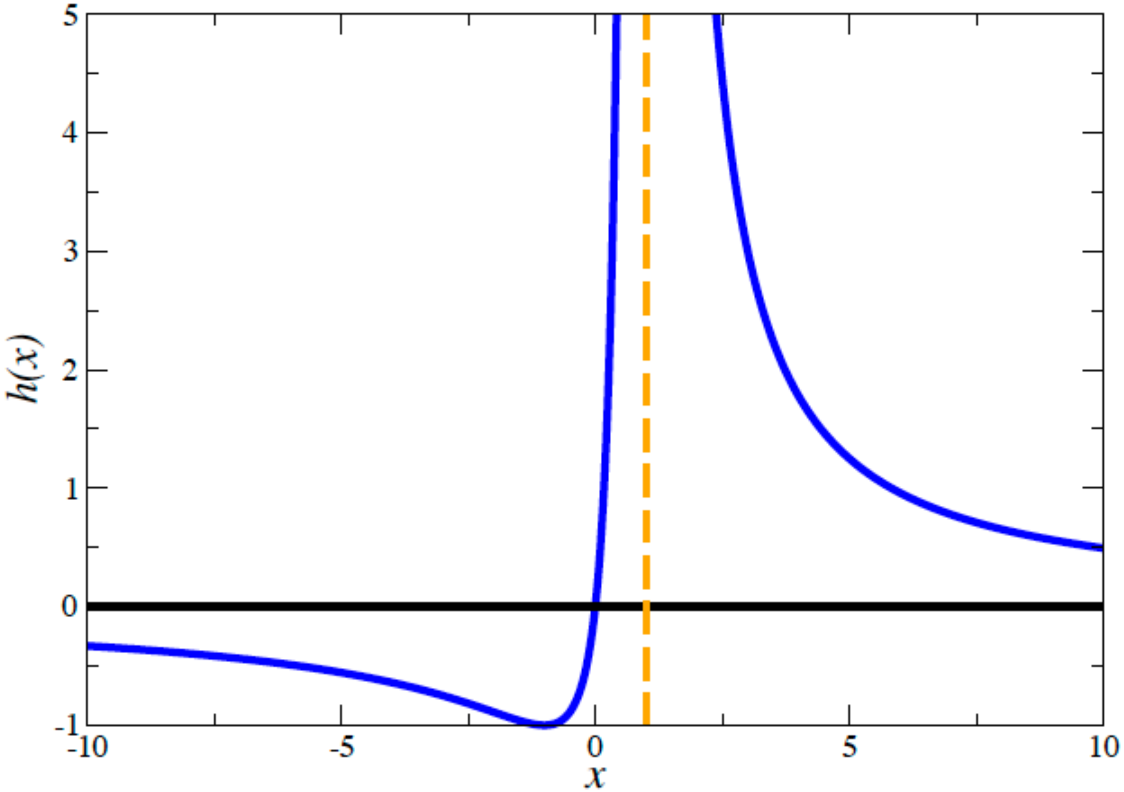
$$\eta(\omega_{\max}) = \frac{\eta_C}{2} \frac{xy}{2+y}$$

At $B = 0$ there is time-reversibility and:

asymmetry parameter $x = 1$

the efficiency only depends on $y(x = 1) = ZT$

$$L_{\rho\rho}L_{qq} - \frac{1}{4}(L_{\rho q} + L_{q\rho})^2 \geq 0 \;\Rightarrow\; \begin{cases} h(x) \leq y \leq 0 & \text{if } x < 0 \\ 0 \leq y \leq h(x) & \text{if } x > 0 \end{cases}$$



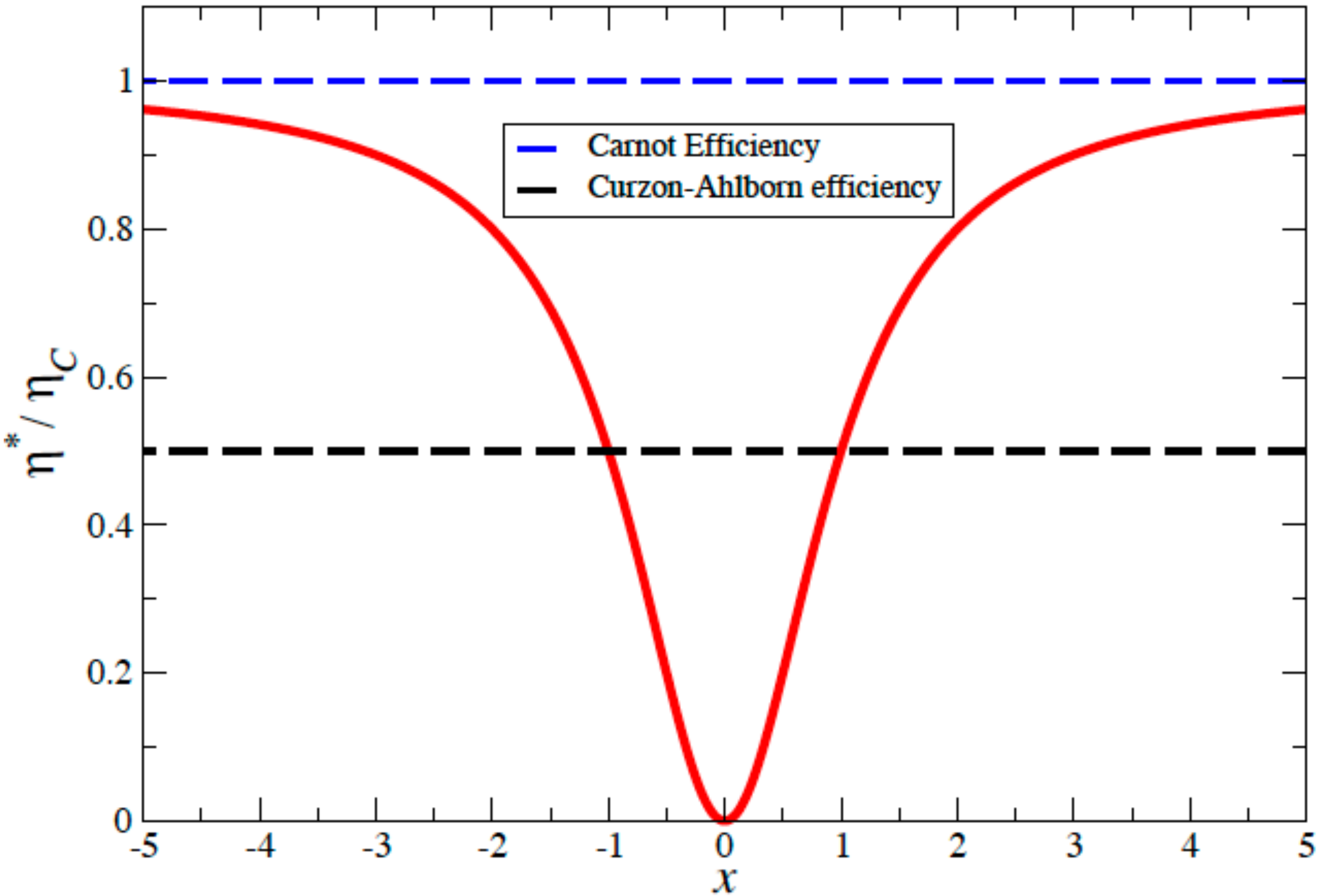
$$h(x) = 4x/(x-1)^2$$

maximum $\eta^\star$ of $\eta(\omega_{\max})$

achieved for $y = h(x)$

$$\eta(\omega_{\max}) \leq \eta^\star = \eta_C \frac{x^2}{x^2+1}$$

The Curzon-Ahlborn limit can be overcome within linear response



MAXIMUM EFFICIENCY

$$\eta = \frac{\Delta\mu J_\rho}{J_q} = \frac{-TX_1(L_{\rho\rho}X_1 + L_{\rho q}X_2)}{L_{q\rho}X_1 + L_{qq}X_2} \qquad (J_q > 0)$$

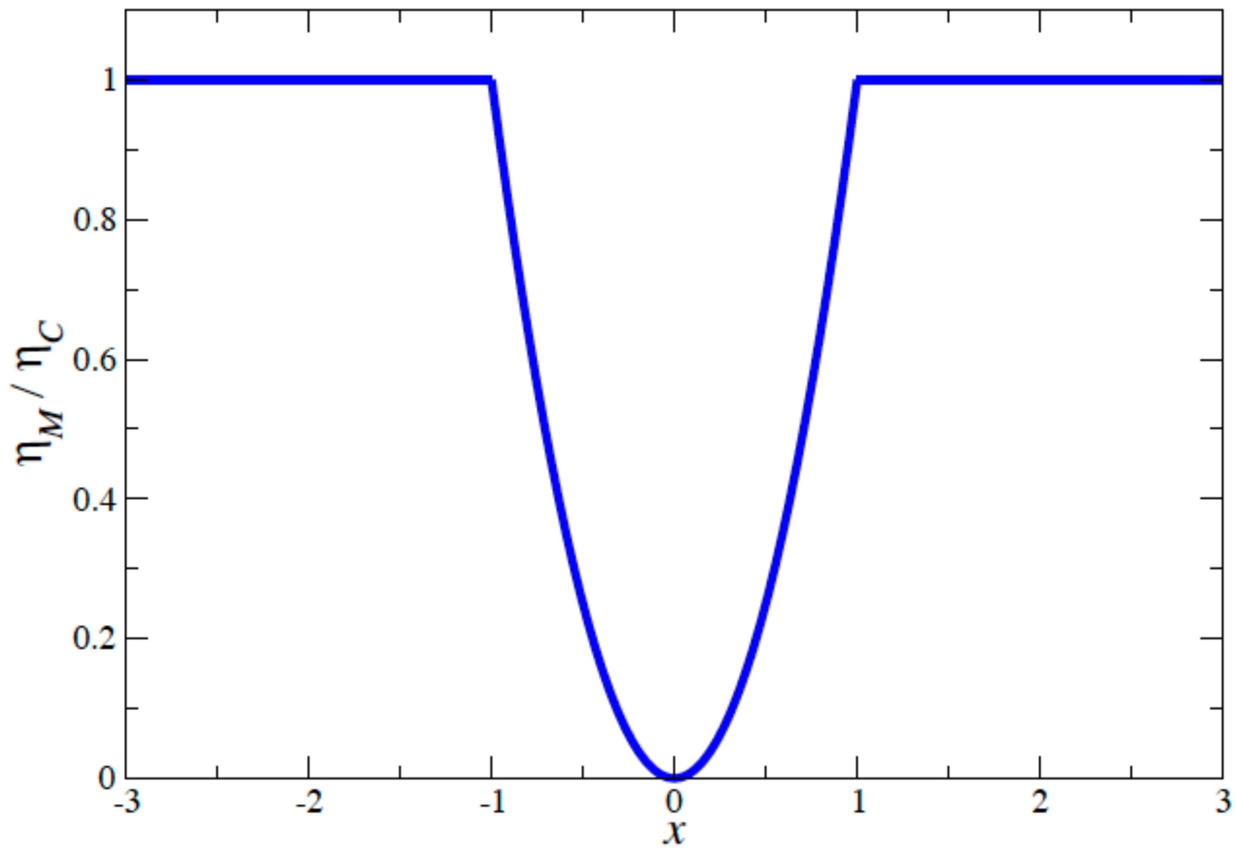
Maximum efficiency achieved for

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

$$\eta_{\max} = \eta_C\, x\, \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1}$$

maximum η_M of $\eta_{\max}$ achieved for $y = h(x)$

$$\eta_M = \begin{cases} \eta_C \, x^2 & \text{if } |x| \le 1 \\ \eta_C & \text{if } |x| \ge 1 \end{cases}$$



The Carnot limit can be achieved only when

$$|x| \ge 1$$

When |x| is large the figure of merit y required to get Carnot efficiency becomes small

<u>Carnot efficiency could be obtained far from the strong coupling condition</u>

Entropy production rate at maximum efficiency

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

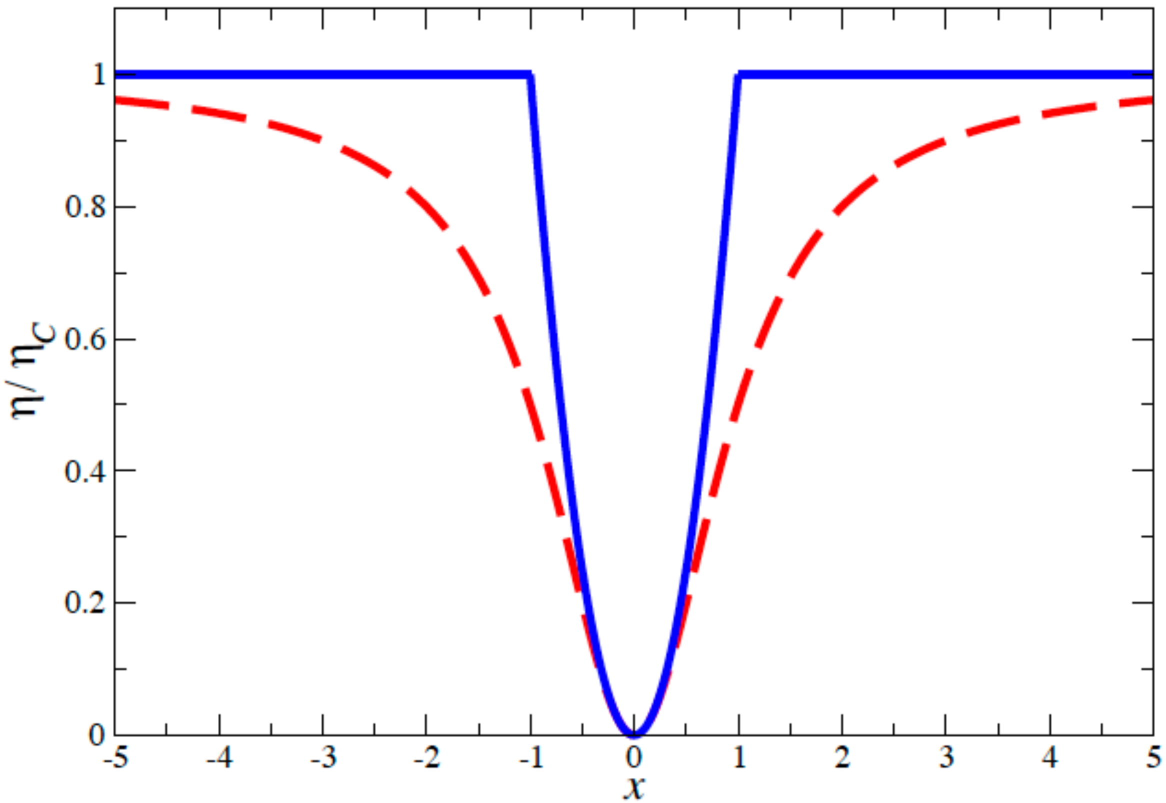
There is no entropy production at |x|>1, in agreement with the fact that in this regime we reach Carnot efficiency

OUTPUT POWER AT MAXIMUM EFFICIENCY

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

When time-reversibility is broken, <u>within linear response</u> is it possible to have simultaneously Carnot efficiency and non-zero power.

Terms of higher order in the entropy production, beyond linear response, will generally be non-zero. However, irrespective how close we are to the Carnot efficiency, we can find small enough forces such that the linear theory holds.



$$\text{when } |x| \to \infty$$

$$\eta^\star \to \eta_M = \eta_C$$

$$\omega(\eta_M) \to \omega_{\max}$$

Maximum power
at the maximum
(Carnot) efficiency

(G.B., K. Saito, G. Casati, PRL **106**, 230602 (2011))

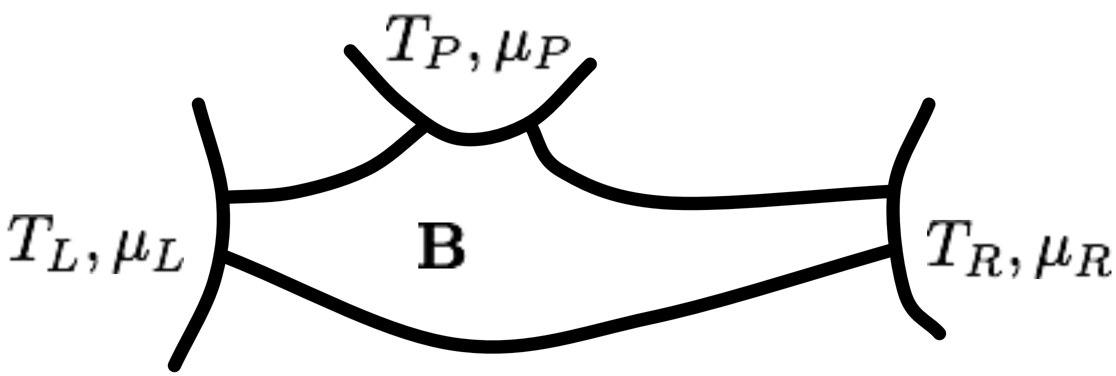
How to obtain asymmetry in the Seebeck coefficient?

For non-interacting systems, due to the symmetry properties of the scattering matrix ⇨ $S(\mathbf{B}) = S(-\mathbf{B})$

This symmetry does not apply when electron-phonon and electron-electron interactions are taken into account

Let us consider the case of partially coherent transport, with inelastic processes simulated by **"conceptual probes"** (Buttiker, 1988).

Non-interacting three-terminal model



P probe reservoir

$$T_L = T + \Delta T, \quad T_R = T$$
$$\mu_L = \mu + \Delta\mu, \quad \mu_R = \mu$$
$$T_P = T + \Delta T_P$$
$$\mu_P = \mu + \Delta\mu_P$$

Charge and energy conservation: $\sum_k J_{\rho,k} = 0,$
$\sum_k J_{E,k} = 0, \quad (k = L, R, P)$

Entropy production (linear response):

$$\dot{S} = {}^t\mathbf{J}\mathbf{X} = \sum_{i=1}^{4} J_i X_i,$$

$${}^t\mathbf{J} = (eJ_{\rho,L}, J_{q,L}, eJ_{\rho,P}, J_{q,P})$$
$${}^t\mathbf{X} = \left(\frac{\Delta\mu}{eT}, \frac{\Delta T}{T^2}, \frac{\Delta\mu_P}{eT}, \frac{\Delta T_P}{T^2}\right)$$
$$(J_{q,k} = J_{E,k} - \mu J_{\rho,k})$$

Three-terminal Onsager matrix

Equation connecting fluxes and thermodynamic forces:

$$\boldsymbol{J} = \boldsymbol{L}\boldsymbol{X}$$

$\boldsymbol{L}$ is a 4×4 Onsager matrix

In block-matrix form:

$$\begin{pmatrix} \boldsymbol{J}_\alpha \\ \boldsymbol{J}_\beta \end{pmatrix} = \begin{pmatrix} \boldsymbol{L}_{\alpha\alpha} & \boldsymbol{L}_{\alpha\beta} \\ \boldsymbol{L}_{\beta\alpha} & \boldsymbol{L}_{\beta\beta} \end{pmatrix} \begin{pmatrix} \boldsymbol{X}_\alpha \\ \boldsymbol{X}_\beta \end{pmatrix}$$

Zero-particle and heat current condition through the probe terminal:

$$\boldsymbol{J}_\beta = (J_3, J_4) = 0 \quad \Rightarrow \quad \boldsymbol{X}_\beta = -\boldsymbol{L}_{\beta\beta}{}^{-1}\boldsymbol{L}_{\beta\alpha}\boldsymbol{X}_\alpha$$

Two-terminal Onsager matrix for partially coherent transport

Reduction to 2x2 Onsager matrix when the third terminal is a probe terminal mimicking phase-breaking.

$$\boldsymbol{J}_\alpha = \boldsymbol{L}_{\alpha\alpha}{}' \boldsymbol{X}_\alpha, \quad \boldsymbol{L}_{\alpha\alpha}{}' \equiv \left(\boldsymbol{L}_{\alpha\alpha} - \boldsymbol{L}_{\alpha\beta} \boldsymbol{L}_{\beta\beta}{}^{-1} \boldsymbol{L}_{\beta\alpha} \right)$$

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} L'_{11} & L'_{12} \\ L'_{21} & L'_{22} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix}$$

$\mathbf{L}'$ is the two-terminal Onsager matrix for partially coherent transport

The Seebeck coefficient is not bounded to be symmetric in $\mathbf{B}$ (for asymmetric structures)

First-principle exact calculation within the Landauer-Büttiker approach

Bilinear Hamiltonian $H = H_S + H_R + H_C$

Tight binding N-site Hamiltonian

$$H_S = \sum_{n,n'=1}^{N} H_{nn'} c_n^\dagger c_n'$$

Reservoirs (ideal Fermi gases): $H_R = \sum_{k,q} E_q c_{kq}^\dagger c_{kq}$

Coupling (tunneling) Hamiltonian

$$H_C = \sum_{k,q} (t_{kq} c_{kq}^\dagger c_{i_k} + t_{kq}^\star c_{kq} c_{i_k}^\dagger)$$

Charge and heat current from the left terminal

$$J_1 = \frac{e}{h}\int dE \sum_k [\tau_{kL}(E) f_L(E) - \tau_{Lk}(E) f_k(E)]$$

$$J_2 = \frac{1}{h}\int dE \sum_k (E-\mu_L)[\tau_{kL}(E) f_L(E) - \tau_{Lk}(E) f_k(E)]$$

$$f_k(E) = \{\exp[(E-\mu_k)/k_B T_k] + 1]^{-1}$$ Fermi function

τ_{kl} transmission probability from terminal l to terminal k

$$J_3 = J_1(L \to P), \quad J_4 = J_2(L \to P)$$

Transmission probabilities:

$$\tau_{pq}(E) = \mathrm{Tr}[\Gamma_p(E)G(E)\Gamma_q(E)G^\dagger(E)]$$

Broadening functions $\Gamma_k(E) \equiv i[\Sigma_k(E) - \Sigma_k^\dagger(E)]$

Self-energies Σ_k

Retarded system's Green function

$$G(E) \equiv [E - H_S - \sum_k \Sigma_k(E)]^{-1}$$

Onsager coefficients from linear response expansion of the currents

$$L_{11} = \frac{e^2}{h} \int dE \sum_{k \neq L} \tau_{Lk}(E) \left[-\frac{\partial f(E)}{\partial E} \right],$$

$$L_{12} = \frac{e}{h} \int dE \, (E-\mu) \sum_{k \neq L} \tau_{Lk}(E) \left[-\frac{\partial f(E)}{\partial E} \right],$$

$$L_{22} = \frac{T}{h} \int dE \, (E-\mu)^2 \sum_{k \neq L} \tau_{Lk}(E) \left[-\frac{\partial f(E)}{\partial E} \right],$$

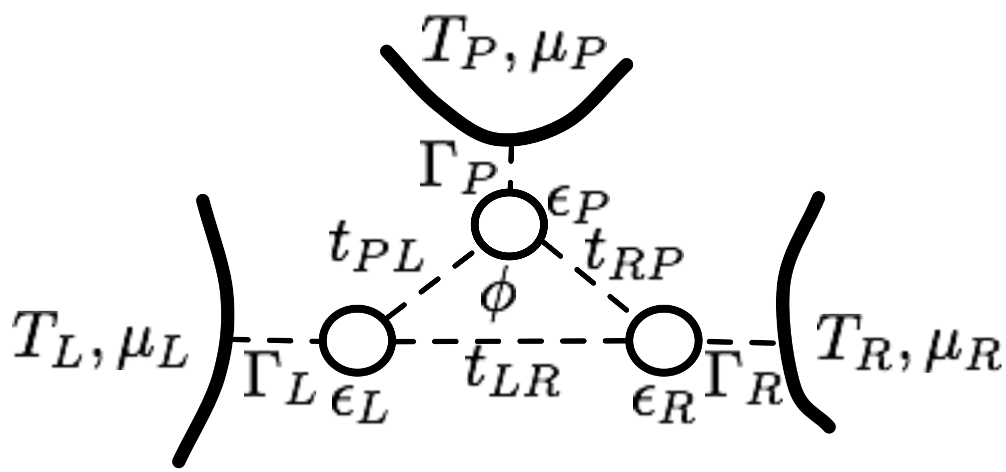
$$L_{21} = L_{12}.$$

Analogous formulas are obtained for L_{33}, $L_{34} = L_{43}$, and L_{44}, with the P terminal used instead of L

$$
\begin{aligned}
L_{13} &= \frac{e^2}{h}\int dE\,\tau_{LP}(E)\left[-\frac{\partial f(E)}{\partial E}\right],\\
L_{14} &= \frac{e}{h}\int dE\,(E-\mu)\tau_{LP}(E)\left[-\frac{\partial f(E)}{\partial E}\right],\\
L_{24} &= \frac{T}{h}\int dE\,(E-\mu)^2\tau_{LP}(E)\left[-\frac{\partial f(E)}{\partial E}\right],\\
L_{23} &= L_{14}.
\end{aligned}
$$

In the other off-diagonal block τ_{PL} appears and we may have $\tau_{PL} \neq \tau_{LP}$

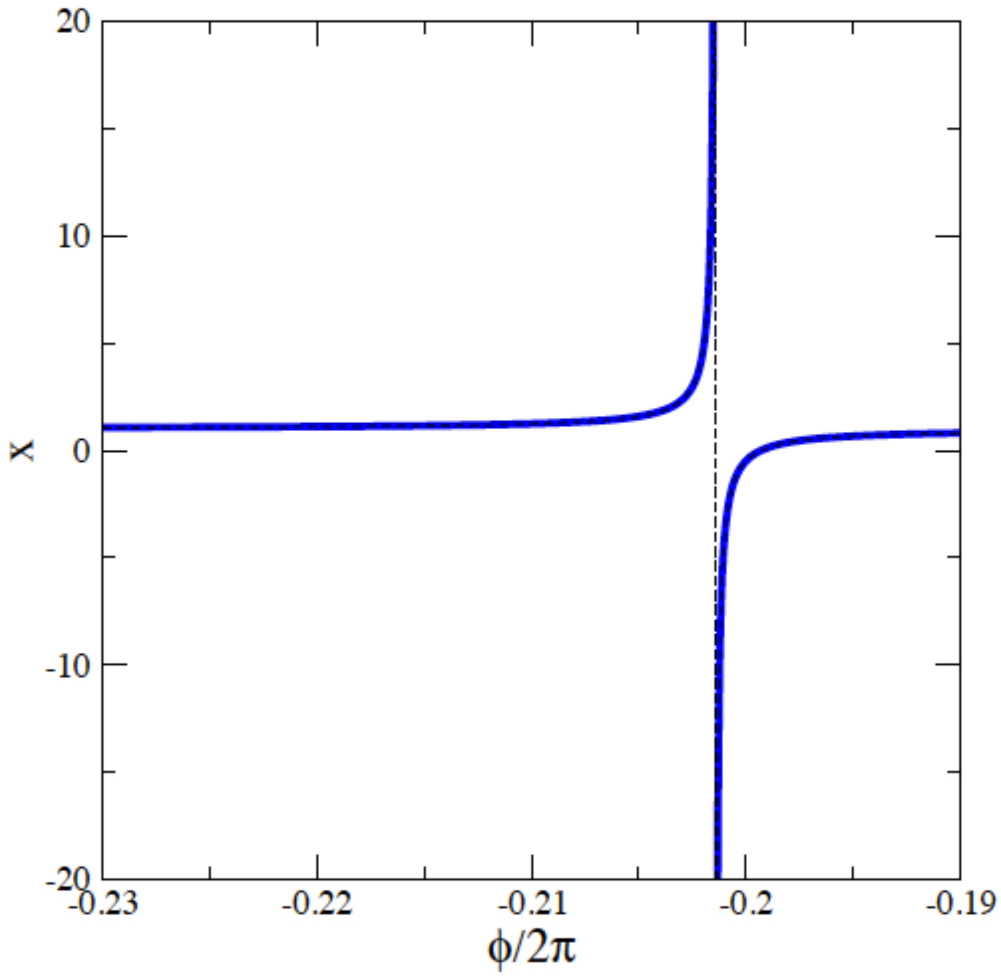
Illustrative three-dot example



$$H_S = \sum_k \epsilon_k c_k^\dagger c_k + (t_{LR} c_R^\dagger c_L e^{i\phi/3} + t_{RP} c_P^\dagger c_R e^{i\phi/3} + t_{PL} c_L^\dagger c_P e^{i\phi/3} + \text{H.c.})$$

Asymmetric structure, e.g.. $\epsilon_L \neq \epsilon_R$

Asymmetric Seebeck coefficient



$$x(\phi) = \frac{L'_{12}(\phi)}{L'_{21}(\phi)} = \frac{S(\phi)}{S(-\phi)} \neq 1$$

(K. Saito, G. B., G. Casati, T. Prosen, PRB **84**, 201306(R) (2011))

(see also D. Sánchez, L. Serra, PRB **84**, 201307(R) (2011))

Asymmetric power generation and refrigeration

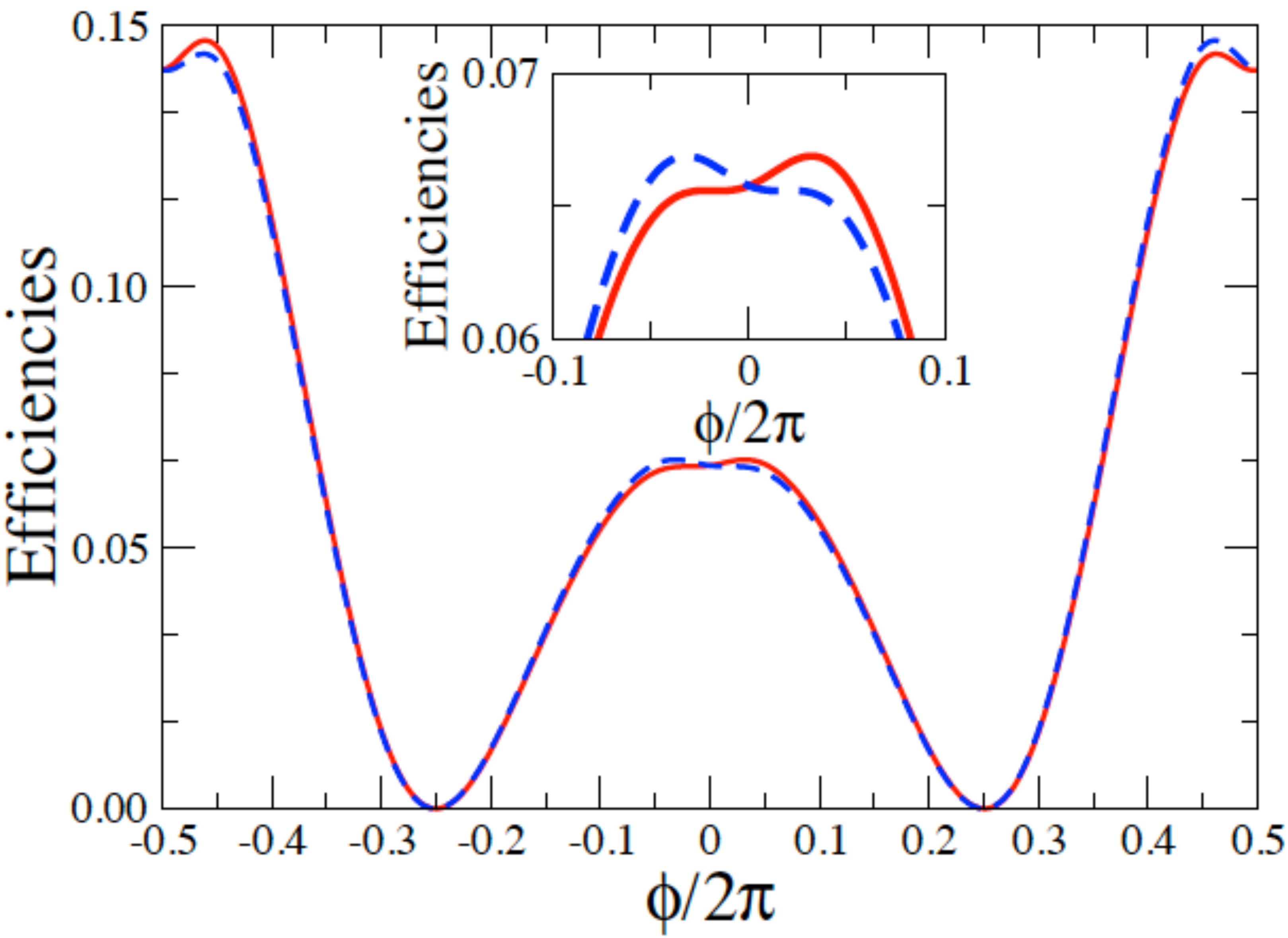
When a magnetic field is added, the efficiencies of power generation and refrigeration are no longer equal:

$$\eta_{\max} = \eta_C \, x \, \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1}, \qquad \eta_{\max}^{(r)} = \eta_C \, \frac{1}{x} \, \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1}$$

To linear order in the applied flux:

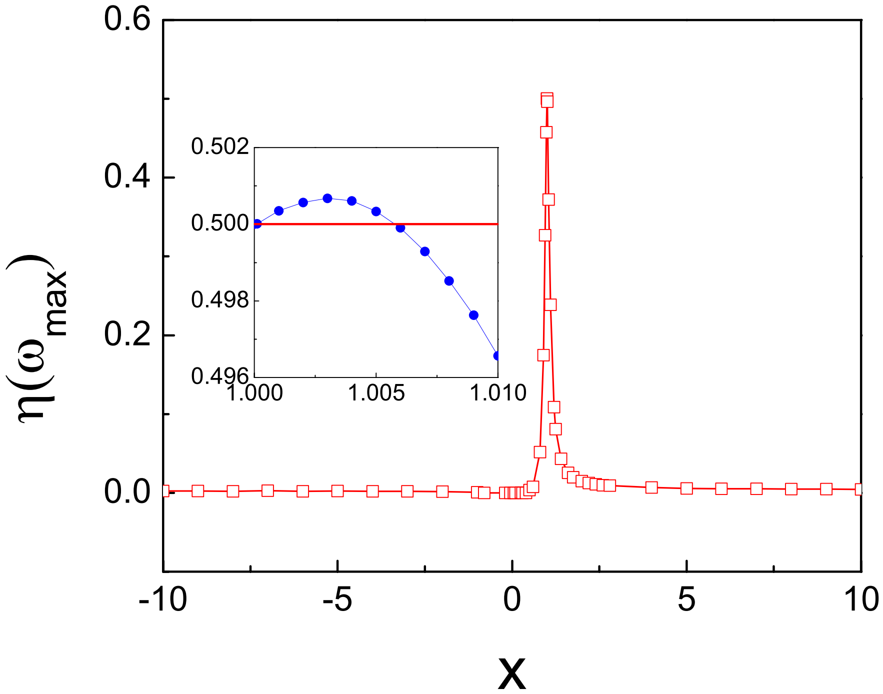
$$\frac{\eta_{\max}(\phi) + \eta_{\max}^{(r)}(\phi)}{2} = \eta_{\max}(0) = \eta_{\max}^{(r)}(0)$$

A small magnetic field improves either power generation or refrigeration, and vice versa if we reverse the direction of the field



The large-field enhancement of efficiencies is model-dependent, but the small-field asymmetry is generic

Optimized efficiency

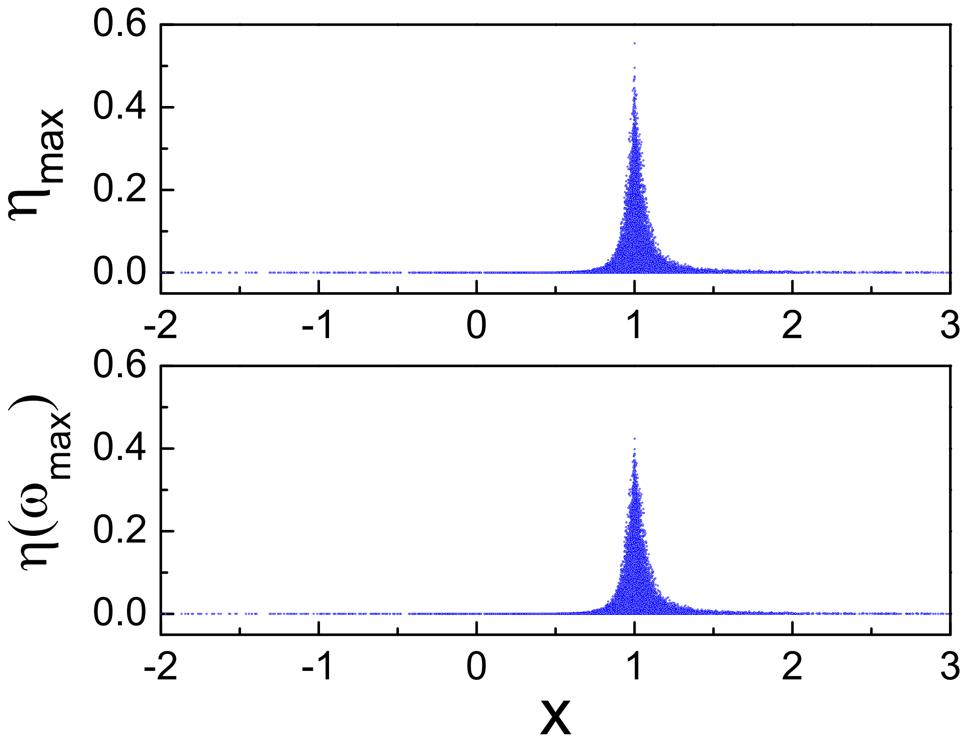


Optimization by means of simulated annealing

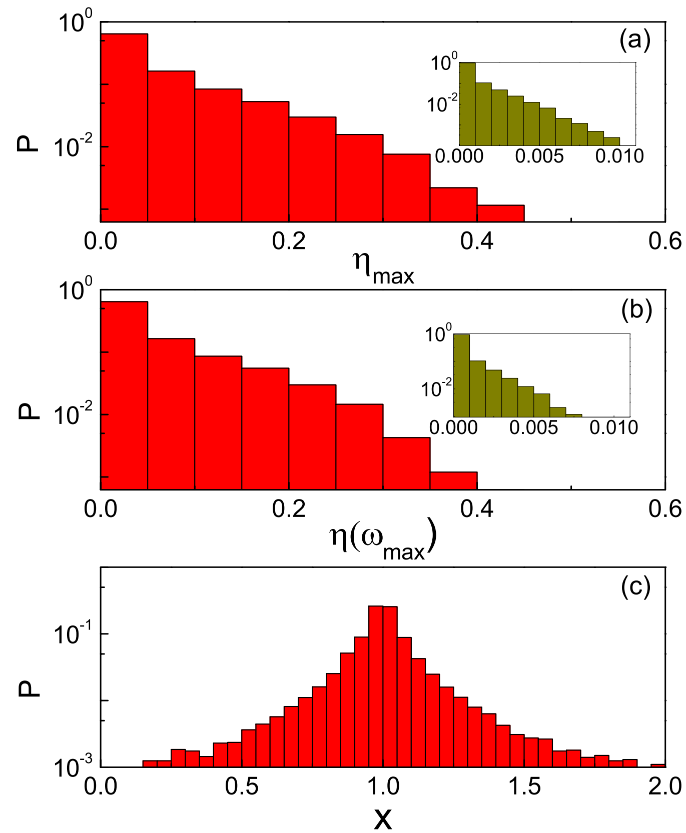
The Curzon-Ahlborn limit can be overcome (within linear response)

(V. Balachandran, G. B., G. Casati, preprint)

Random matrix (GUE) model



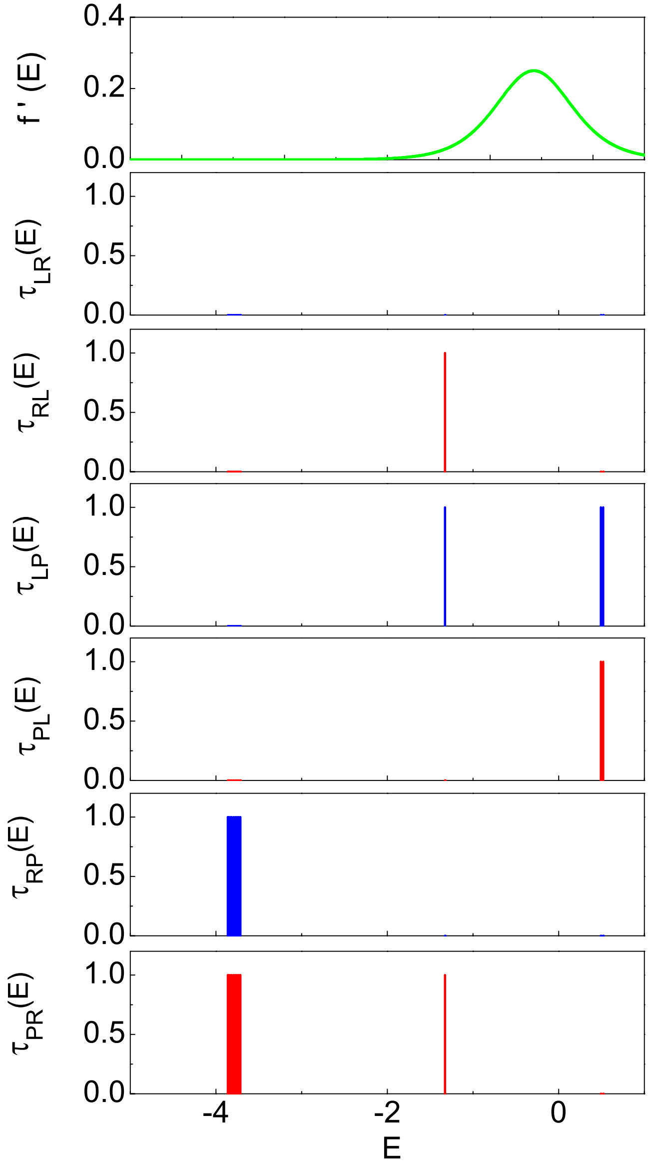
It is highly improbable to obtain large asymmetries and large efficiencies

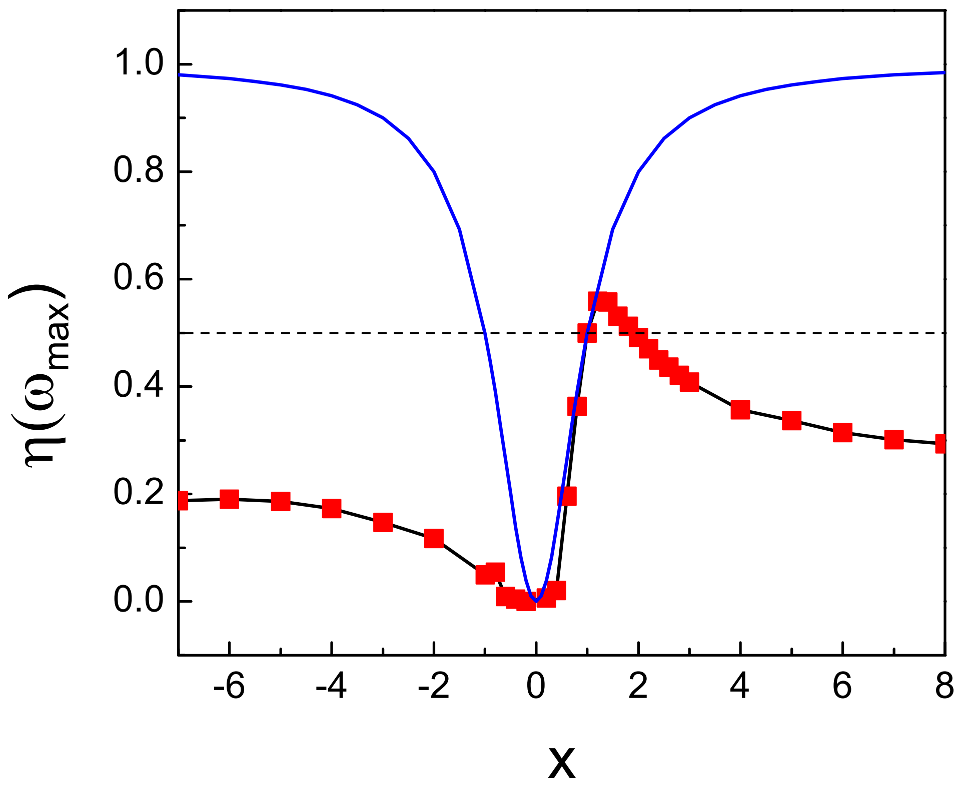


(V. Balachandran, G. B., G. Casati, preprint)

Transmission windows model

$$\sum_i \tau_{ij}(E) = \sum_j \tau_{ij}(E) = 1$$





(V. Balachandran, G. B., G. Casati, preprint; se also M. Horvat, T. Prosen, G. B., G. Casati, arXiv:1207.6014)

Summary

When time-reversal symmetry is broken new thermodynamic bounds on thermoelectric efficiencies are needed.

Carnot efficiency in principle achievable far from the strong coupling regime $J_\rho \propto J_q$ and with finite power (within linear response)

The Curzon-Ahlborn limit can be overcome within linear response

For partially coherent transport in asymmetric structures the Seebeck coefficient is not an even function of the field

Asymmetric efficiencies of power generation and refrigeration

The non-interacting cases studied so far exhibit strongly asymmetric thermopower but with low efficiencies.
Is this result generic, also beyond linear response and for interacting systems?