Theoretical approaches for nanoscale thermoelectric phenomena

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Fundamental aspects of steady-state conversion of heat to work at the nanoscale

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Giuliano Benenti [a,b,*], Giulio Casati [a,c], Keiji Saito [d], Robert S. Whitney [e]

Quantum computation and information is a rapidly developing interdisciplinary field. It is not easy to understand its fundamental concepts and central results without facing numerous technical details. This book provides the reader with a useful guide. In particular, the initial chapters offer a simple and self-contained introduction; no previous knowledge of quantum mechanics or classical computation is required.

Various important aspects of quantum computation and information are covered in depth, starting from the foundations (the basic concepts of computational complexity, energy, entropy, and information, quantum superposition and entanglement, elementary quantum gates, the main quantum algorithms, quantum teleportation, and quantum cryptography) up to advanced topics (like entanglement measures, quantum discord, quantum noise, quantum channels, quantum error correction, quantum simulators, and tensor networks).

It can be used as a broad range textbook for a course in quantum information and computation, both for upper-level undergraduate students and for graduate students. It contains a large number of solved exercises, which are an essential complement to the text, as they will help the student to become familiar with the subject. The book may also be useful as general education for readers who want to know the fundamental principles of quantum information and computation.

"Thorough introductions to classical computation and irreversibility, and a primer of quantum theory, lead into the heart of this impressive and substantial book. All the topics – quantum algorithms, quantum error correction, adiabatic quantum computing and decoherence are just a few – are explained carefully and in detail. Particularly attractive are the connections between the conceptual structures and mathematical formalisms, and the different experimental protocols for bringing them to practice. A more wide-ranging, comprehensive, and definitive text is hard to imagine."

— Sir Michael Berry, *University of Bristol, UK*

"This second edition of the textbook is a timely and very comprehensive update in a rapidly developing field, both in theory as well as in the experimental implementation of quantum information processing. The book provides a solid introduction into the field, a deeper insight in the formal description of quantum information as well as a well laid-out overview on several platforms for quantum simulation and quantum computation. All in all, a well-written and commendable textbook, which will prove very valuable both for the novices and the scholars in the fields of quantum computation and information."

— Rainer Blatt, *Universität Innsbruck and IQOQI Innsbruck, Austria*

"The book by Benenti, Casati, Rossini and Strini is an excellent introduction to the fascinating field of quantum information, of great benefit for scientists entering the field and a very useful reference for people already working in it. The second edition of the book is considerably extended with new chapters, as the one on many-body systems, and necessary updates, most notably on the physical implementations."

— Rosario Fazio, *The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy*

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Benenti
Casati
Rossini
Strini

Principles of Quantum Computation and Information
A Comprehensive Textbook

Giuliano Benenti Giulio Casati
Davide Rossini Giuliano Strini

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A	R	E	P	O
T	E	N	E	T
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Principles of Quantum Computation and Information

A Comprehensive Textbook

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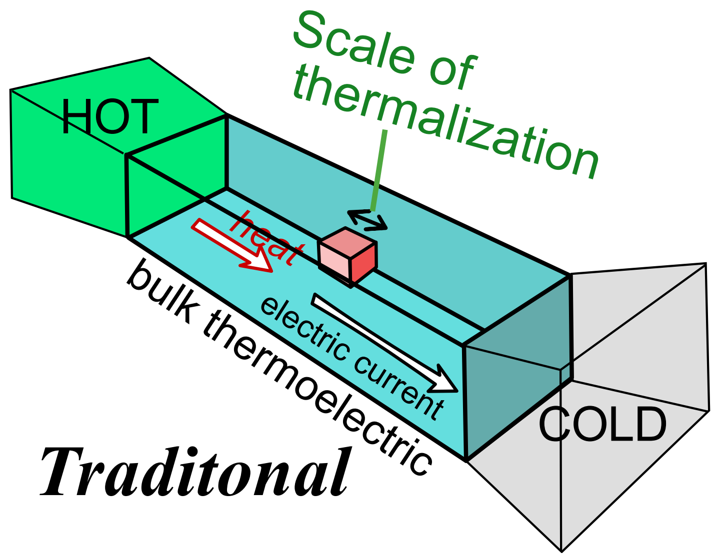
Outline

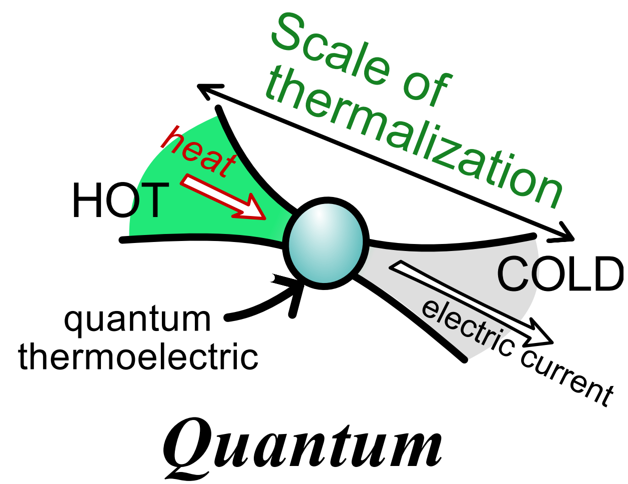
1) Thermoelectricity in the quantum coherent regime
(scattering theory, Landauer formula, energy filtering)

2) Thermoelectricity in the Coulomb blockade regime
(quantum dot model, kinetic equations)

3) Aspects of thermoelectricity in strongly interacting systems
(phase transitions, power-efficiency trade-off, power-efficiency-fluctuations trade-off)

Traditional versus quantum thermoelectrics



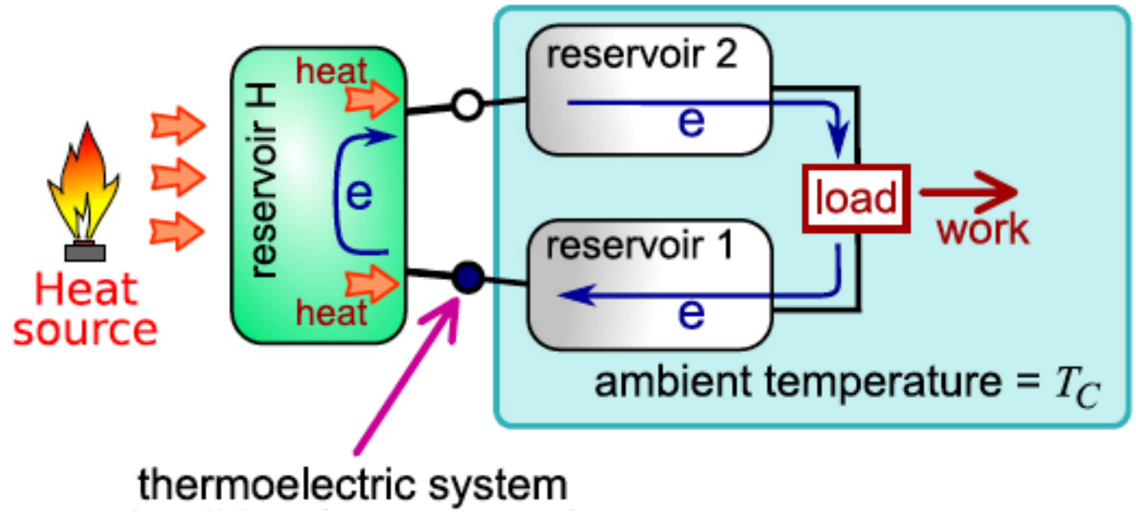


Relaxation length (tens of nanometers at room temperature) of the order of the mean free path; inelastic scattering (phonons) thermalizes the electrons

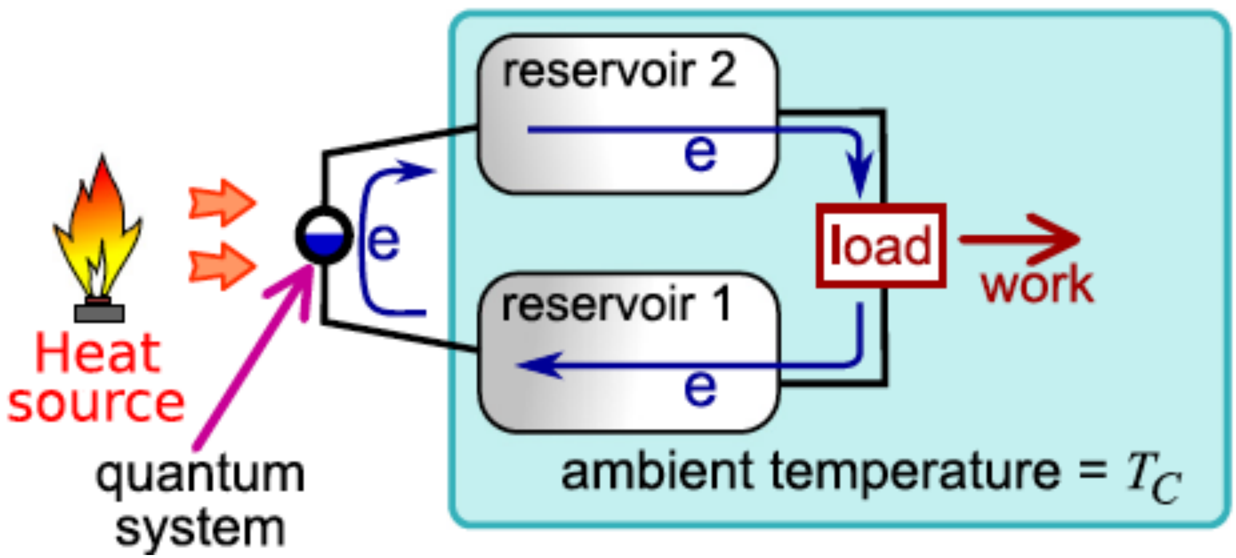
Structures smaller than the relaxation length (many microns at low temperature); quantum interference effects; Boltzmann transport theory cannot be applied; efficiency depends on geometry and size

[see G. B., G. Casati, K. Saito, R. S. Whitney, Phys. Rep. **694**, 1 (2017)]

Traditional thermocouple



Quantum thermocouple



Noninteracting systems,
Energy filtering,
Landauer scattering theory

Proc. Natl. Acad. Sci. USA
Vol. 93, pp. 7436–7439, July 1996
Applied Physical Sciences

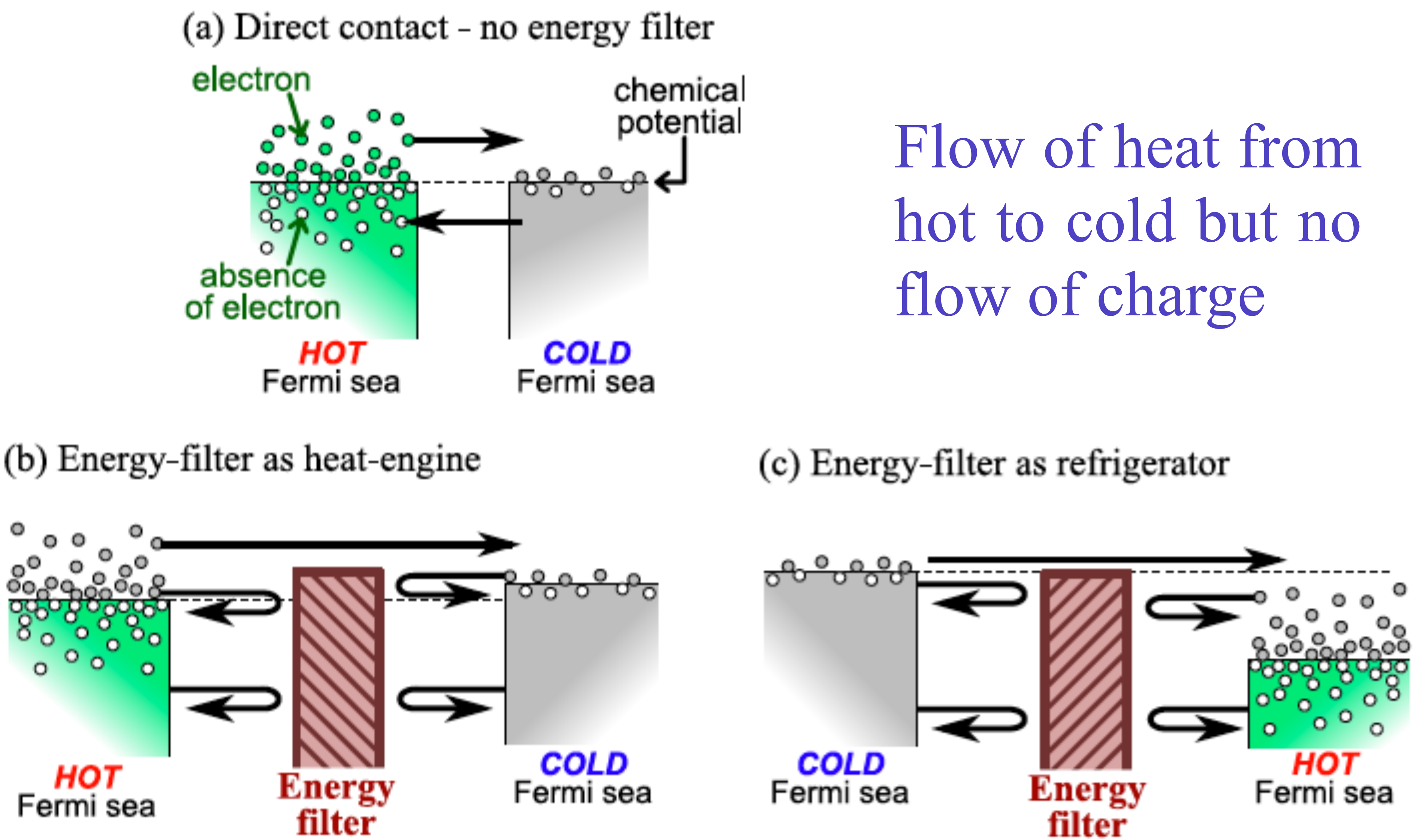
This contribution is part of a special series of Inaugural Articles by members of the National Academy of Sciences elected on April 25, 1995.

The best thermoelectric

G. D. MAHAN*† AND J. O. SOFO‡

ABSTRACT What electronic structure provides the largest figure of merit for thermoelectric materials? To answer that question, we write the electrical conductivity, thermopower, and thermal conductivity as integrals of a single function, the transport distribution. Then we derive the mathematical function for the transport distribution, which gives the largest figure of merit. A delta-shaped transport distribution is found to maximize the thermoelectric properties. This result indicates that a narrow distribution of the energy of the electrons participating in the transport process is needed for maximum thermoelectric efficiency. Some possible realizations of this idea are discussed.

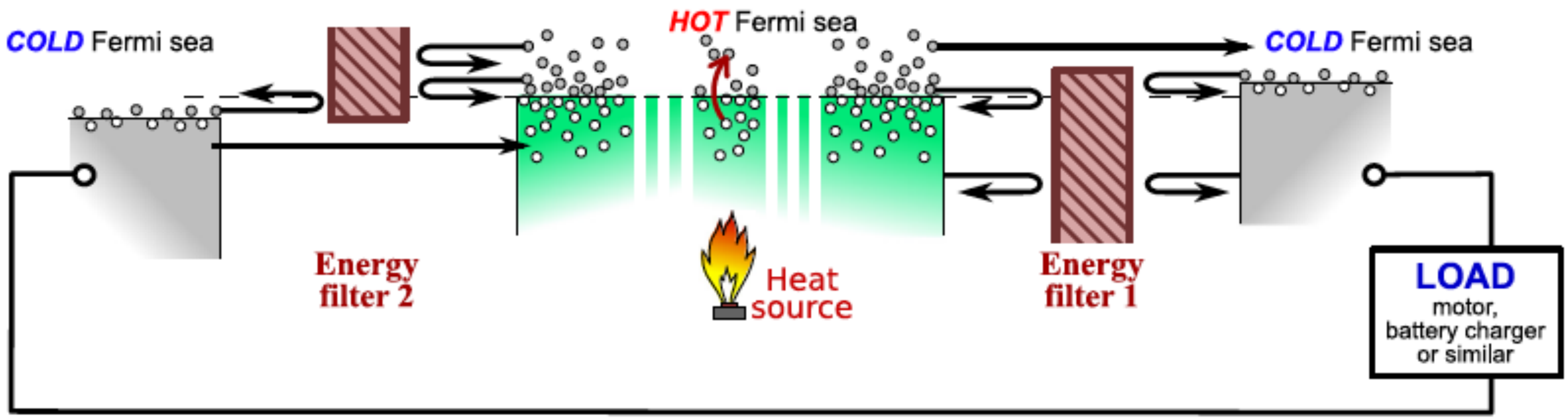
Heat-to-work conversion through energy filtering



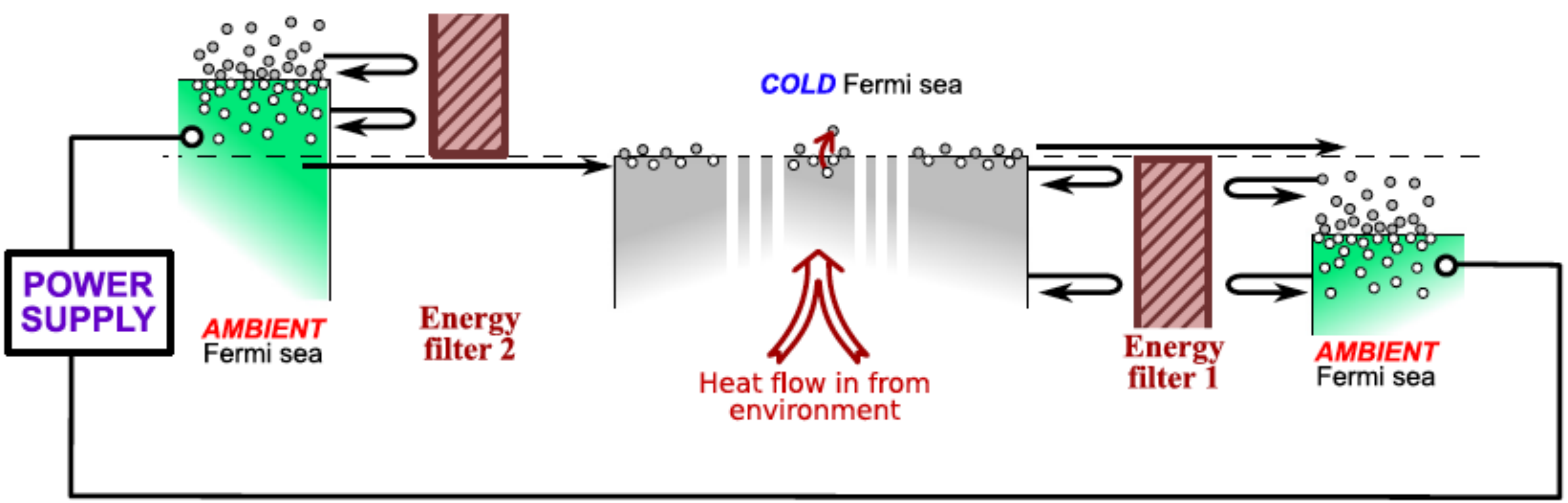
Flow of heat from hot to cold but no flow of charge

[see G. B., G. Casati, K. Saito, R. S. Whitney, Phys. Rep. **694**, 1 (2017)]

Energy filters in a thermocouple geometry

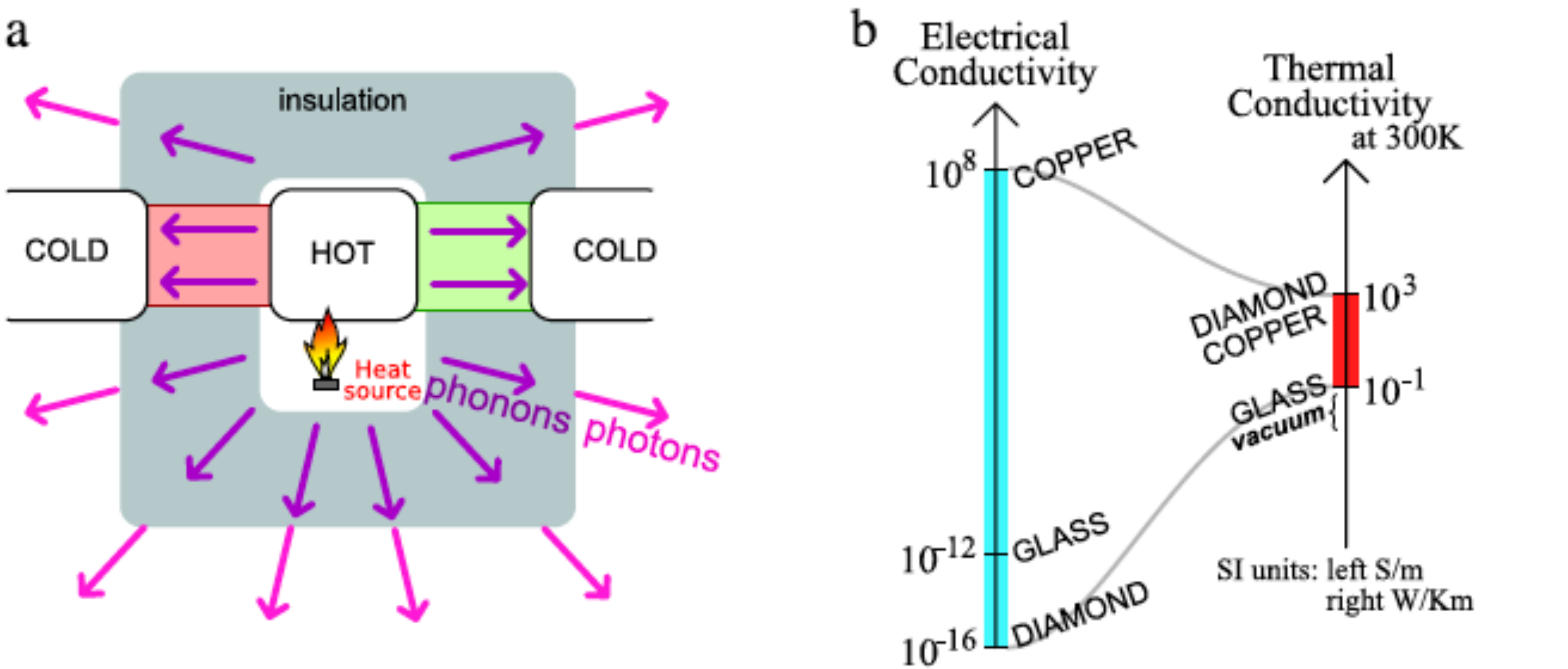


(a) Thermocouple (pair of thermoelectrics) as heat-engine.



(b) Thermocouple (pair of thermoelectrics) as refrigerator.

What about phonons?



$$\eta_{\text{eng}} = \frac{P_{\text{gen}}}{J^{(\text{el})}_{\text{h,H}} + J^{(\text{ph})}_{\text{h,H}}} \qquad \eta_{\text{eng}} \leq \eta^{\text{Carnot}}_{\text{eng}} \times \frac{J^{(\text{el})}_{\text{H}}}{J^{(\text{el})}_{\text{H}} + J^{(\text{ph})}_{\text{H}}}$$

Necessary both: (i) to reduce phonon transport; (ii) to have an efficient working fluid (optimize the electron dynamics)

Reducing thermal conductance

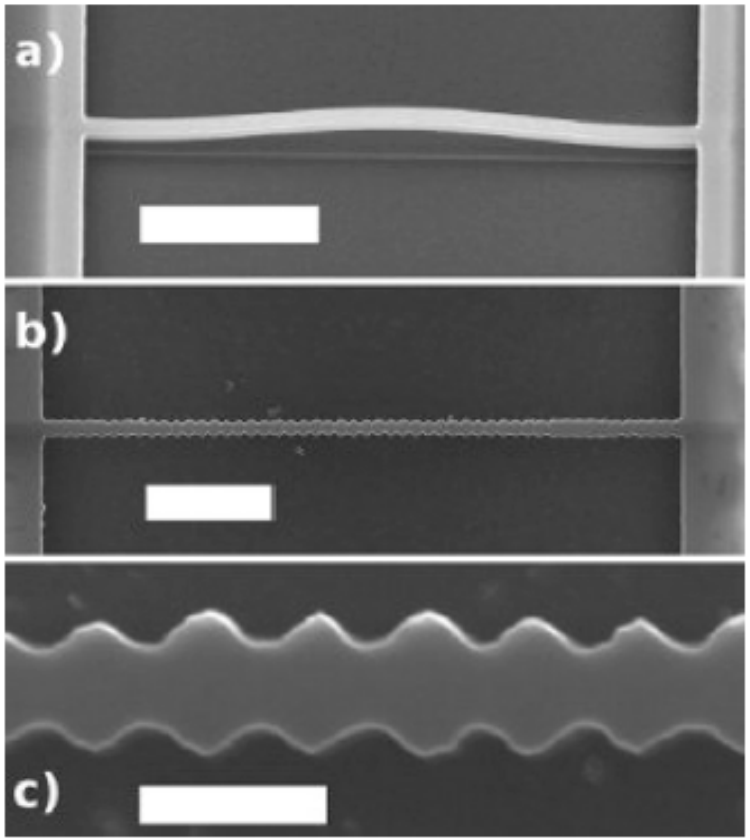


FIG. 1. SEM images of the straight (a) and the corrugated (b) nanowires; (c) corresponds to the top view of the corrugated nanowire. The scale bars correspond to (a) 2 μm, (b) 2 μm, and (c) 300 nm.

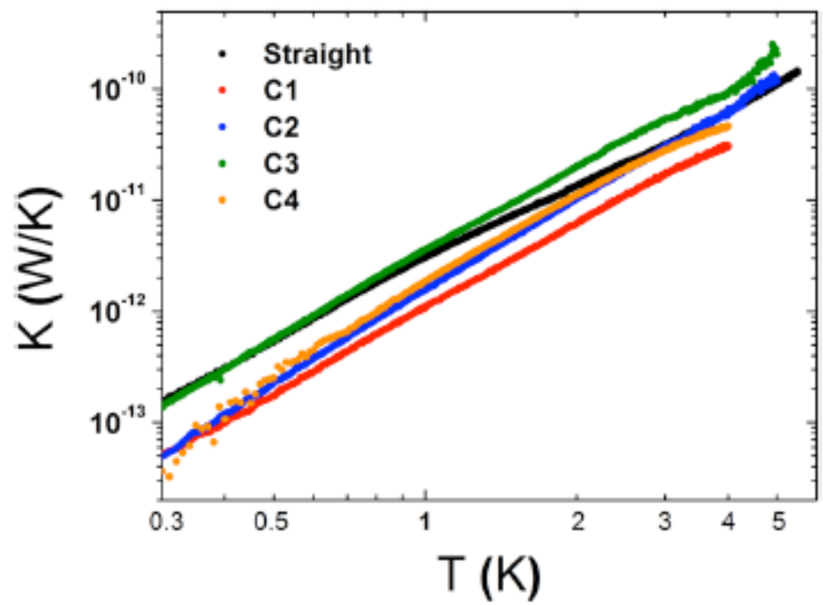
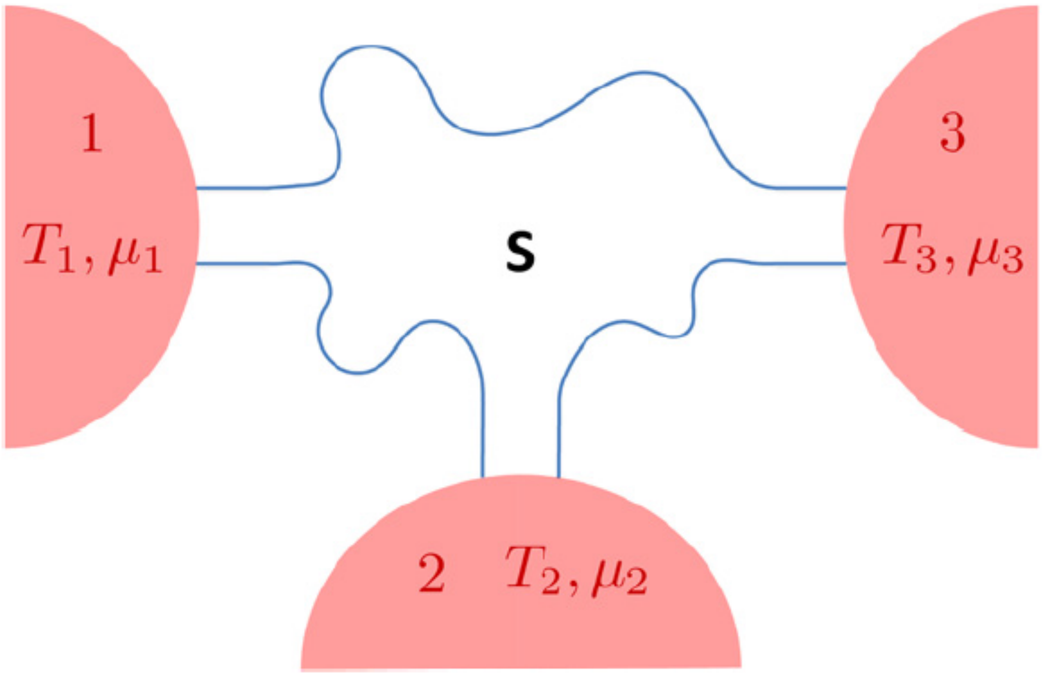


FIG. 2. Thermal conductance versus temperature for a straight nanowire and four corrugated nanowires in the log-log scale.

[Blanc, Rajabpour, Volz, Fournier, Bourgeois, APL **103**, 043109 (2013)]

Scattering theory



Scattering region connected to N terminals (reservoirs)

Describes elastic scattering (including the effect of a disorder potential), but not electron-electron interactions beyond Hartree approximation and electron-phonon interactions

Transmission matrix

Probability for an electron with energy E to go from (transverse) mode m of reservoir j to mode n of reservoir i:

$$P_{in;jm}(E) = \left|\mathcal{S}_{in;jm}(E)\right|^2$$

$\mathcal{S}_{in;jm}(E)$ scattering matrix elements

$$\mathcal{T}_{ij}(E) = \sum_{nm} P_{in;jm}(E)$$

transmission matrix elements

probabilities $\mathcal{T}_{ij}(E) \geq 0$ for all i, j, E

From conservation of current and condition of zero current at zero bias:

$$\sum_i \mathcal{T}_{ij}(E) = N_j(E), \quad \sum_j \mathcal{T}_{ij}(E) = N_i(E)$$

From time reversal symmetry of the scatterer Hamiltonian:

$$\mathcal{S}_{in;jm}(E, -\mathbf{B}) = \mathcal{S}^*_{jm;in}(E, \mathbf{B}), \quad \mathcal{T}_{ij}(E, \mathbf{B}) = \mathcal{T}_{ji}(E, -\mathbf{B})$$

Landauer approach

Electrical current into the scatterer from reservoir i:

$$J_{e,i} = \sum_j \int_{-\infty}^{\infty} \frac{\mathrm{d}E}{h}\, e\, \left[N_i(E)\,\delta_{ij} - \mathcal{T}_{ij}(E)\right] f_j(E)$$

Fermi function $\quad f_i(E) = \left(1 + \exp\left[(E-\mu_i)/(k_\mathrm{B}T_i)\right]\right)^{-1}, \quad \mu_i = eV_i$

Energy current into the scatterer from reservoir i:

$$J_{u,i} = \sum_j \int_{-\infty}^{\infty} \frac{\mathrm{d}E}{h}\, E\, \left[N_i(E)\,\delta_{ij} - \mathcal{T}_{ij}(E)\right] f_j(E)$$

$\Delta Q_i = E - \mu_i \quad$ heat carried by an electron leaving reservoir i

Heat current: $\quad J_{h,i} = \sum_j \int_{-\infty}^{\infty} \frac{\mathrm{d}E}{h} (E-\mu_i) \left[N_i(E)\,\delta_{ij} - \mathcal{T}_{ij}(E)\right] f_j(E).$

Kirkhoff's law of current conservation for (steady state) electrical and energy currents:

$$\sum_i J_{e,i} = \sum_i J_{u,i} = 0$$

Heat current not conserved:

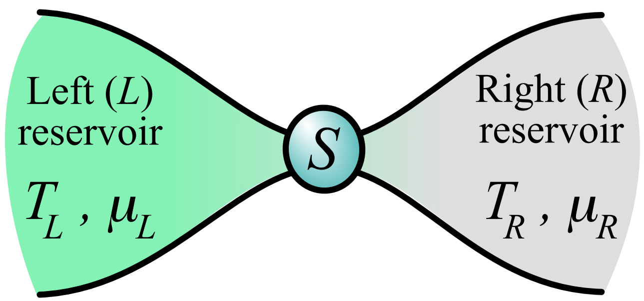
$$J_{h,i} = J_{u,i} - V_i J_{e,i}, \quad \sum_i J_{h,i} = -\sum_i V_i J_{e,i} \qquad P_{\mathrm{gen}} = -\sum_i V_i J_{e,i}$$

Heat dissipated in the reservoirs: entropy production rate

$$\dot{\mathscr{S}} = -\sum_i J_{h,i}/T_i$$

Heat (not energy) current gauge invariant

Two-terminal (thermoelectric) power production



$$\eta = \frac{P}{J_{h,L}}$$

$$P = [(\mu_R - \mu_L)/e]J_e$$

$$(T_L > T_R,\ \mu_L < \mu_R) \qquad P, J_{h,L} > 0$$

The upper bound to efficiency is given by the Carnot efficiency (expected only at zero power; intuitively, finite currents entail dissipation): $\eta_C = 1 - \dfrac{T_R}{T_L}$

Scattering theory for two reservoirs

$$\mathcal{T}_{LR}(E) = \mathcal{T}_{RL}(E) \geq 0, \quad \mathcal{T}_{LL}(E) = N_L(E) - \mathcal{T}_{LR}(E)$$

Conserved currents:

$$J_{e,L} = -J_{e,R} = \int_{-\infty}^{\infty} \frac{\mathrm{d}E}{h}\, e\, \mathcal{T}_{LR}(E)\, [f_L(E) - f_R(E)]\,,$$

$$J_{u,L} = -J_{u,R} = \int_{-\infty}^{\infty} \frac{\mathrm{d}E}{h}\, E\, \mathcal{T}_{LR}(E)\, [f_L(E) - f_R(E)]\,.$$

Heat currents:

$$J_{h,L} = \int_{-\infty}^{\infty} \frac{\mathrm{d}E}{h}\, (E - \mu_L)\, \mathcal{T}_{LR}(E)\, [f_L(E) - f_R(E)]\,,$$

$$J_{h,R} = \int_{-\infty}^{\infty} \frac{\mathrm{d}E}{h}\, (E - \mu_R)\, \mathcal{T}_{LR}(E)\, [f_R(E) - f_L(E)]\,,$$

First law of thermodynamics: $J_{h,L} + J_{h,R} = (V_R - V_L) J_{e,L}$

Thermoelectric efficiency (power production)

Charge current $J_e = eJ_\rho = \frac{e}{h}\int_{-\infty}^{\infty} dE\tau(E)[f_L(E) - f_R(E)]$

Heat current from reservoirs:

$$J_{h,\alpha} = \frac{1}{h}\int_{-\infty}^{\infty} dE(E-\mu_\alpha)\tau(E)[f_L(E) - f_R(E)]$$

Efficiency:

$$\eta = \frac{P}{J_{h,L}} \quad (T_L > T_R) \; (\mu_R > \mu_L) \; P, J_{h,L} > 0$$

$$\eta = \frac{[(\mu_R - \mu_L)/e]J_e}{J_{\mathrm{h,L}}} = \frac{(\mu_R - \mu_L)\int_{-\infty}^{\infty} dE\tau(E)[f_L(E) - f_R(E)]}{\int_{-\infty}^{\infty} dE(E-\mu_L)\tau(E)[f_L(E) - f_R(E)]}$$

Delta-energy filtering and Carnot efficiency

If transmission is possible only inside a tiny energy window around E=$E_\star$ then

$$\eta = \frac{\mu_L - \mu_R}{E_\star - \mu_L}$$

In the limit $J_\rho \to 0$, corresponding to reversible transport

$$\frac{E_\star - \mu_L}{T_L} = \frac{E_\star - \mu_R}{T_R} \Rightarrow E_\star = \frac{\mu_R T_L - \mu_L T_R}{T_L - T_R}$$

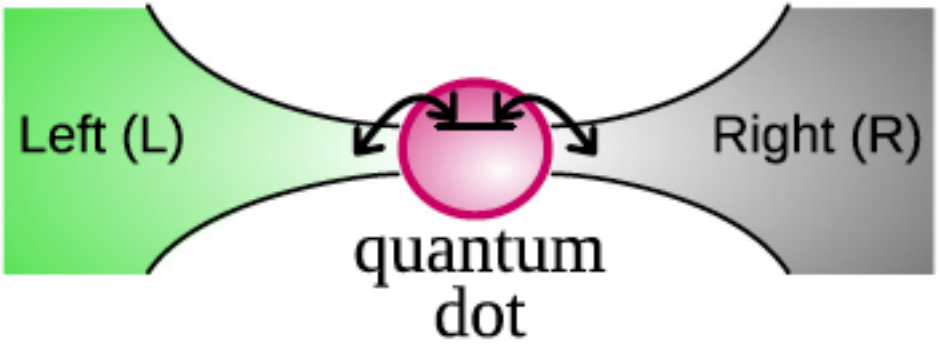
$$\eta = \eta_C = 1 - T_R/T_L$$

Carnot efficiency

Carnot efficiency obtained in the limit of reversible transport (zero entropy production) and zero output power

[Mahan and Sofo, PNAS 93, 7436 (1996);
Humphrey et al., PRL 89, 116801 (2002)]

Example: single-level quantum dot



Dot's scattering matrix:

$$\mathcal{S}(E) = \hat{1} - i2\pi \hat{W}^{\dagger}\left[E - \hat{\mathcal{H}}_{\text{dot}} + i\pi \hat{W}\hat{W}^{\dagger}\right]^{-1}\hat{W}$$

The Green's function is for a non-Hermitian effective Hamiltonian taking into account coupling to the dots

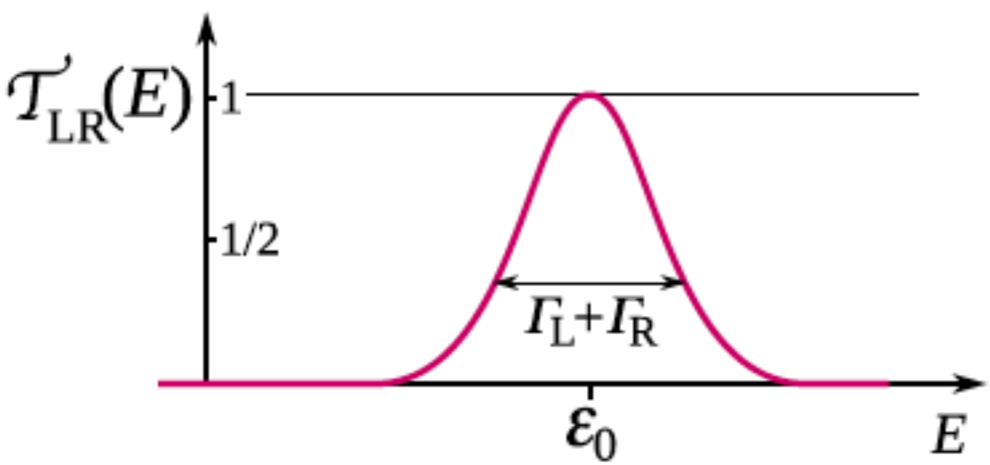
$\hat{W}$ operator coupling the single-level dot to reservoirs:

$$\hat{W} = (w_L, w_R), \qquad \hat{W}^{\dagger} = \begin{pmatrix} w_L^* \\ w_R^* \end{pmatrix}$$

$$\mathcal{S}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{\mathrm{i}2\pi}{E - E_0 + i\pi|w_L|^2 + i\pi|w_R|^2} \begin{pmatrix} |w_L|^2 & w_L^* w_R \\ w_R^* w_L & |w_R|^2 \end{pmatrix}$$

$$\mathit{\Gamma}_i = 2\pi|w_i|^2 \text{ for } i \in L, R,$$

$\mathit{\Gamma}_i/\hbar$ is the rate at which the dot state decays into reservoir i.



$$\mathcal{T}_{LR}(E) = \frac{\mathit{\Gamma}_L \mathit{\Gamma}_R}{(E - E_0)^2 + \frac{1}{4}(\mathit{\Gamma}_L + \mathit{\Gamma}_R)^2}$$

Short intermezzo: Cyclic thermal machines

The upper bound to efficiency is given by the Carnot efficiency:

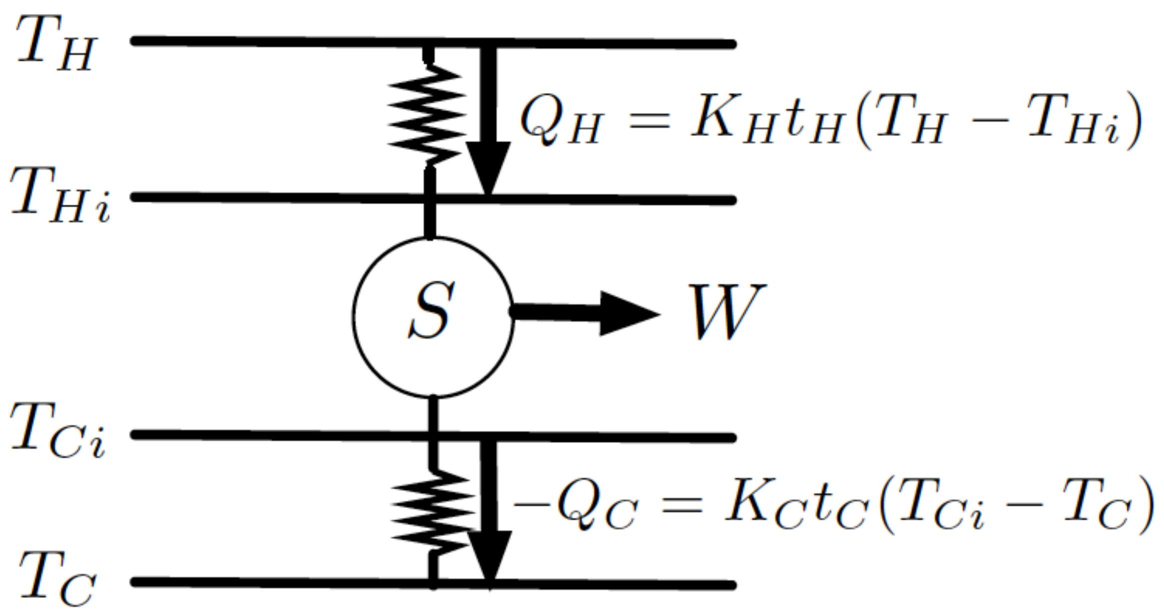
$$\eta = \frac{W}{Q_H} \leq \eta_C = 1 - \frac{T_C}{T_H} \qquad (T_H > T_C)$$

Carnot efficiency obtained for quasi-static transformation (zero extracted power)

The ideal Carnot engine is a reversible machine, since there is no dissipation (no entropy production)

Finite-time thermodynamics I: endoreversible cyclic engines

Dissipation is due to finite thermal conductances between heat reservoirs and the ideal heat engine



S is considered as a Carnot engine operating between the internal temperatures T_{Hi} and T_{Ci} ($T_H > T_{Hi} > T_{Ci} > T_C$)

$$1 - T_{Ci}/T_{Hi} = 1 + Q_C/Q_H$$

Output power:

$$P = \frac{W}{t} = \frac{Q_H + Q_C}{t} = \frac{K_H K_C \alpha\beta(T_H - T_C - \alpha - \beta)}{K_H \alpha T_C + K_C \beta T_H + \alpha\beta(K_H - K_C)}$$

Optimize power with respect to

$$\alpha = T_H - T_{Hi}$$
$$\beta = T_{Ci} - T_C$$

$$T_{Hi} = c\sqrt{T_H}, \quad T_{Ci} = c\sqrt{T_C}, \qquad c \equiv \frac{\sqrt{K_H T_H} + \sqrt{K_C T_C}}{\sqrt{K_H} + \sqrt{K_C}}$$

$$P_{\max} = K_H K_C \left(\frac{\sqrt{T_H} - \sqrt{T_C}}{\sqrt{K_H} + \sqrt{K_C}} \right)^2$$

The efficiency at maximum power (Curzon-Ahlborn efficiency) is independent of the heat conductances:

$$\eta_{CA} = 1 - \sqrt{\frac{T_H}{T_C}} = 1 - \sqrt{1 - \eta_C}$$

[Yvon, 1955; Chambadal, 1957; Novikov, 1958; Curzon and Ahlborn, Am. J. Phys. 43, 22 (1975)]

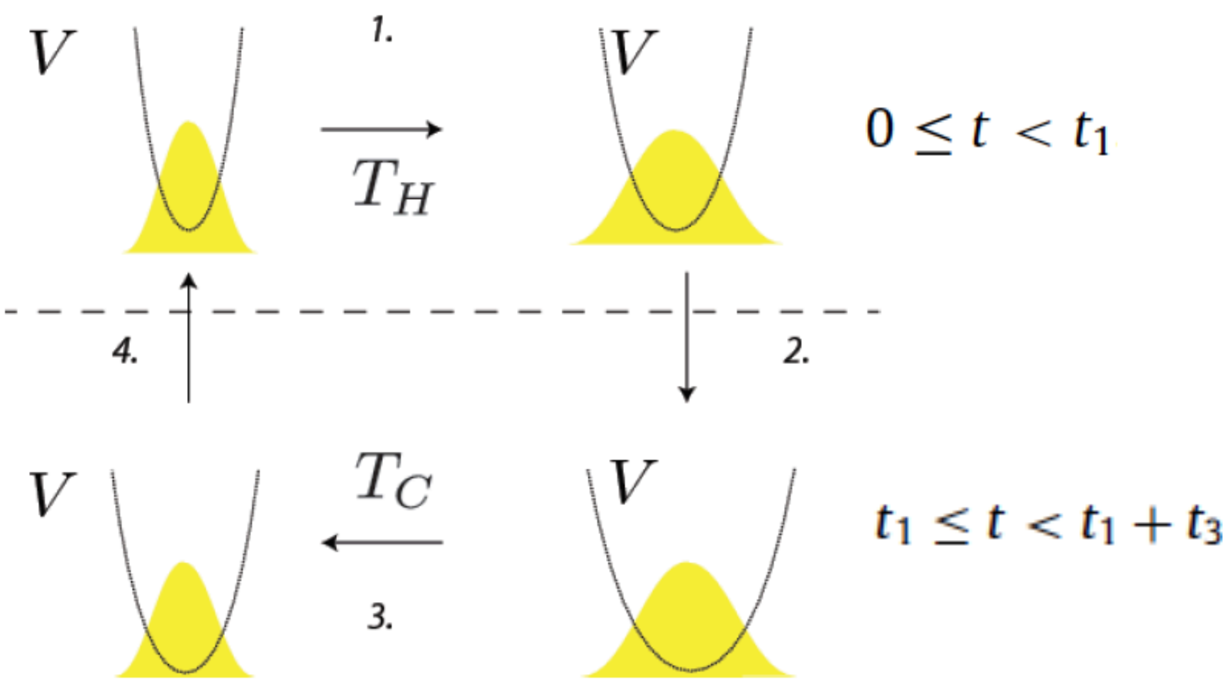
Within linear response: $\eta_{CA} = \dfrac{\eta_C}{2}$

Finite-time thermodynamics II: exoreversible cyclic engines

Irreversibility only arises due to internal dissipative processes

Stochastic thermodynamics

[Seifert, Rep. Prog. Phys. 75, 126001 (2012)]



Time-dependent trapping potential $V(x, \lambda(t)) = \lambda(t)x^2/2$

Time-dependent probability density $p(x, t)$

Fokker-Planck equation:

$$\frac{\partial}{\partial t}p(x,t) \quad = \quad \mu\left(\lambda(t)\frac{\partial}{\partial x}x + T\frac{\partial^2}{\partial x^2}\right)p(x,t)$$

μ is the mobility

Gaussian distribution $p(x,t)$

Exactly solvable model

Schmiedl-Seifert efficiency at maximum power:

$$\eta_{SS} = \frac{\eta_C}{2 - \gamma \eta_C}$$

$\gamma \in [0, 1]$ related to the ratio of entropy production during the hot and cold isothermal steps of the cycle

$\gamma = 1/2$. for the symmetric case

[Schmiedl and Seifert, EPL 81, 20003 (2008)]

Within linear response: $\eta_{CA} = \frac{\eta_C}{2}$

Low-dissipation engines

The entropy production vanishes in the limit of infinite-time cycles:

$$Q_H = T_H\left(\Delta\mathscr{S} - \frac{\Sigma_H}{t_H}\right), \quad Q_C = T_C\left(-\Delta\mathscr{S} - \frac{\Sigma_C}{t_C}\right)$$

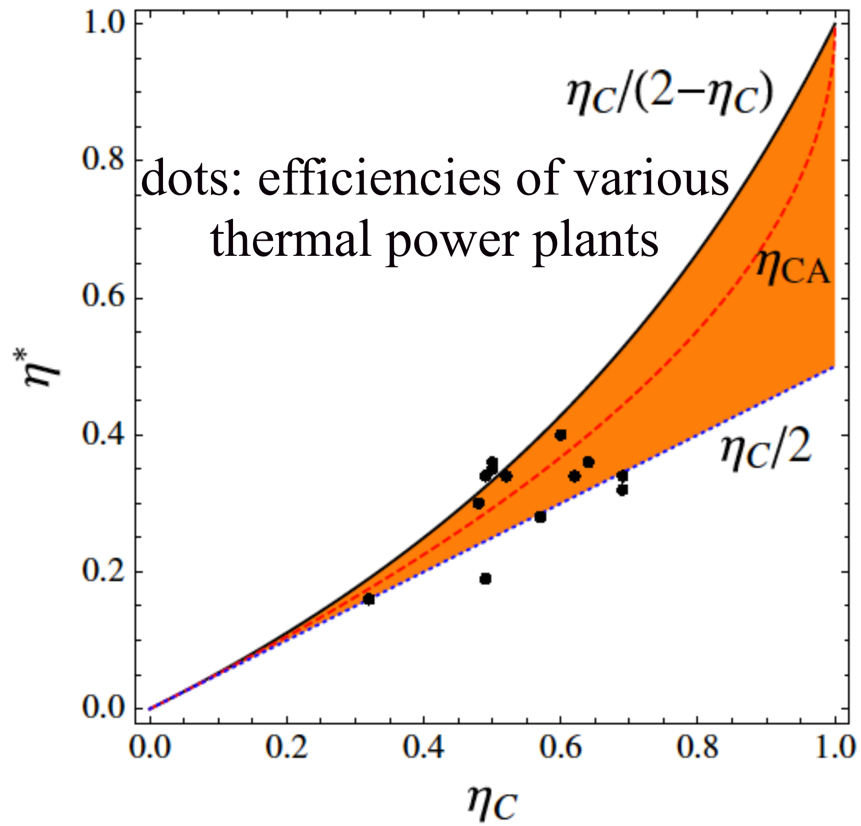
$$P = \frac{Q_H + Q_C}{t_H + t_C} = \frac{(T_H - T_C)\Delta\mathscr{S} - T_H\Sigma_H/t_H - T_C\Sigma_C/t_C}{t_H + t_C}$$

$$\eta(P_{\max}) = \frac{\eta_C\left(1 + \sqrt{\frac{T_C\Sigma_C}{T_H\Sigma_H}}\right)}{\left(1 + \sqrt{\frac{T_C\Sigma_C}{T_H\Sigma_H}}\right)^2 + \frac{T_C}{T_H}\left(1 - \frac{\Sigma_C}{\Sigma_H}\right)}$$

$$\eta_- = \frac{\eta_C}{2} \le \eta(P_{\max}) \le \eta_+ = \frac{\eta_C}{2-\eta_C}$$

$\Sigma_C/\Sigma_H \to \infty$ $\qquad\qquad$ $\Sigma_C/\Sigma_H \to 0$

The CA limit is recovered for symmetric dissipation: $\Sigma_H = \Sigma_C$



[Esposito, Kawai, Lindenberg, Van den Broeck, PRL 105, 150603 (2010)]

Bekenstein-Pendry bound

There is an purely quantum upper bound on the heat current through a single transverse mode

[Bekenstein, PRL **46**, 923 (1981); Pendry, JPA **16**, 2161 (1983)]

For a reservoir coupled to another reservoir at T=0 through a $\mathcal{N}$-mode constriction which lets particle flow at all energies:

$$J_{h,i}^{\max} = \frac{\pi^2}{6h} \mathcal{N} \, k_{\mathrm{B}}^2 T_i^2$$

Maximum power of a heat engine

Since the heat flow must be less than the Bekenstein-Pendry bound and the efficiency smaller than Carnot efficiency also the output power must be bounded

Within scattering theory:

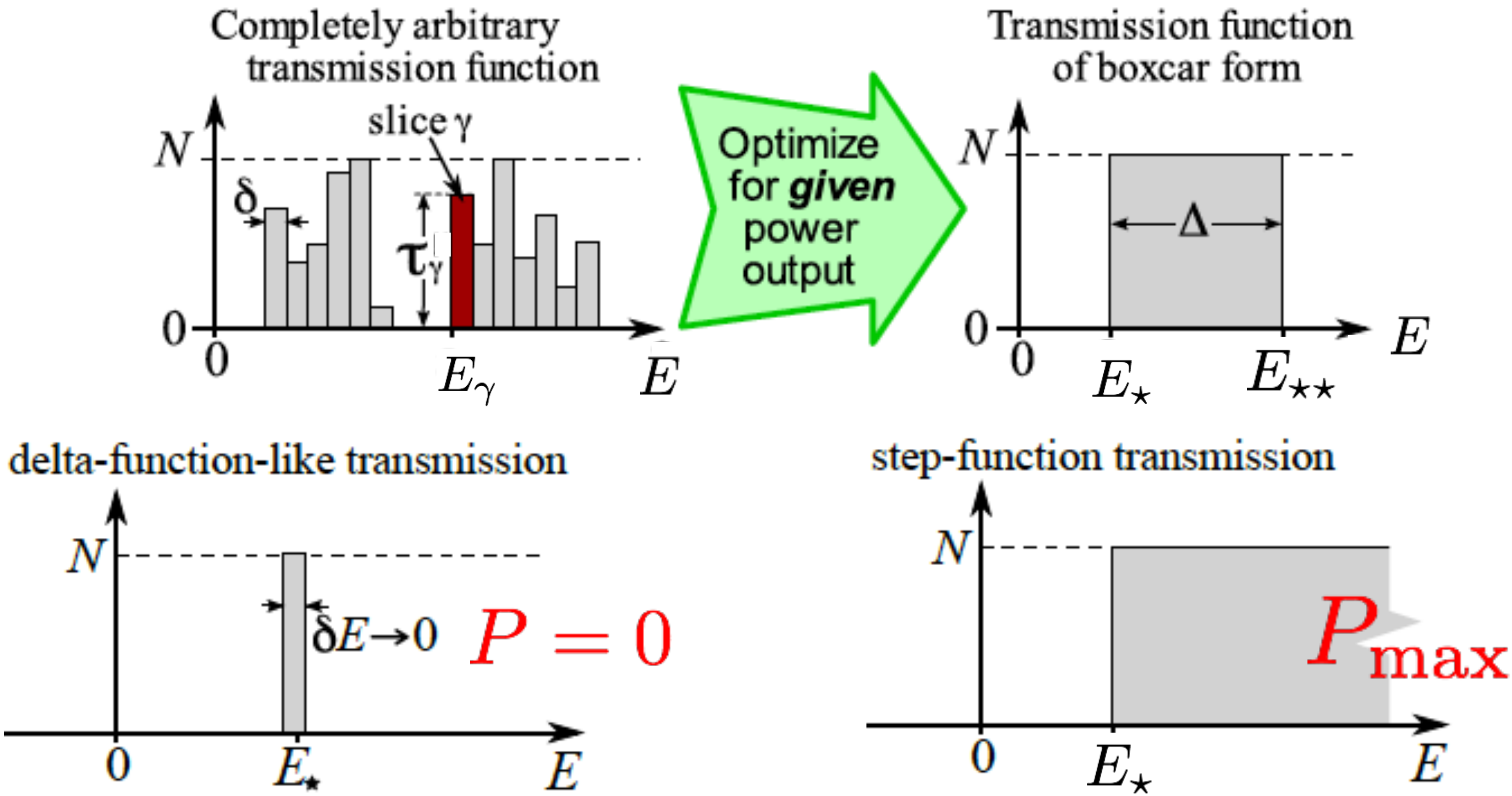
$$P \leq P_{\max} = A_q \frac{\pi^2}{h} \mathcal{N} k_B^2 (\Delta T)^2, \qquad A_q \approx 0.0321,$$

$$\Delta T = T_L - T_R$$

[Whitney, PRL **112**, 130601 (2014); PRB **91**, 115425 (2015)]

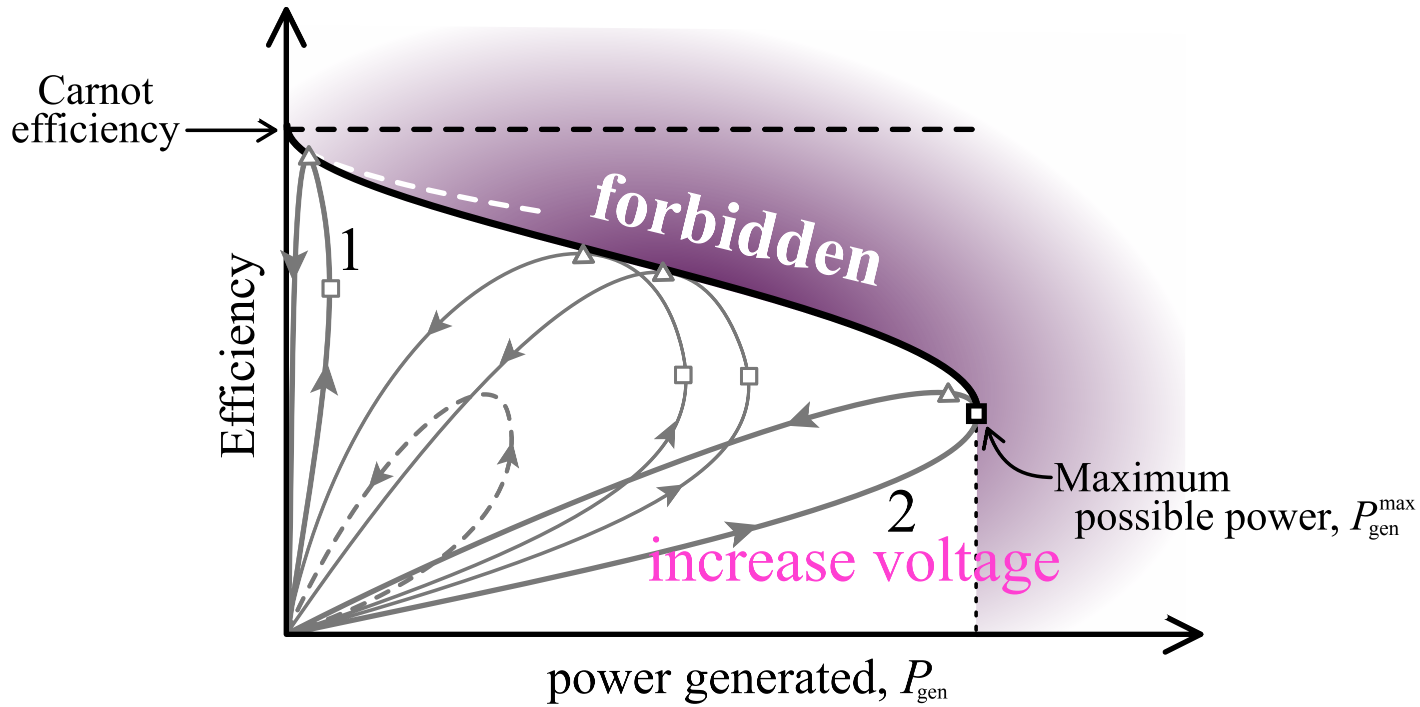
Efficiency optimization (at a given power)

Find the transmission function that optimizes the heat-engine efficiency for a given output power



[Whitney, PRL **112**, 130601 (2014); PRB **91**, 115425 (2015)]

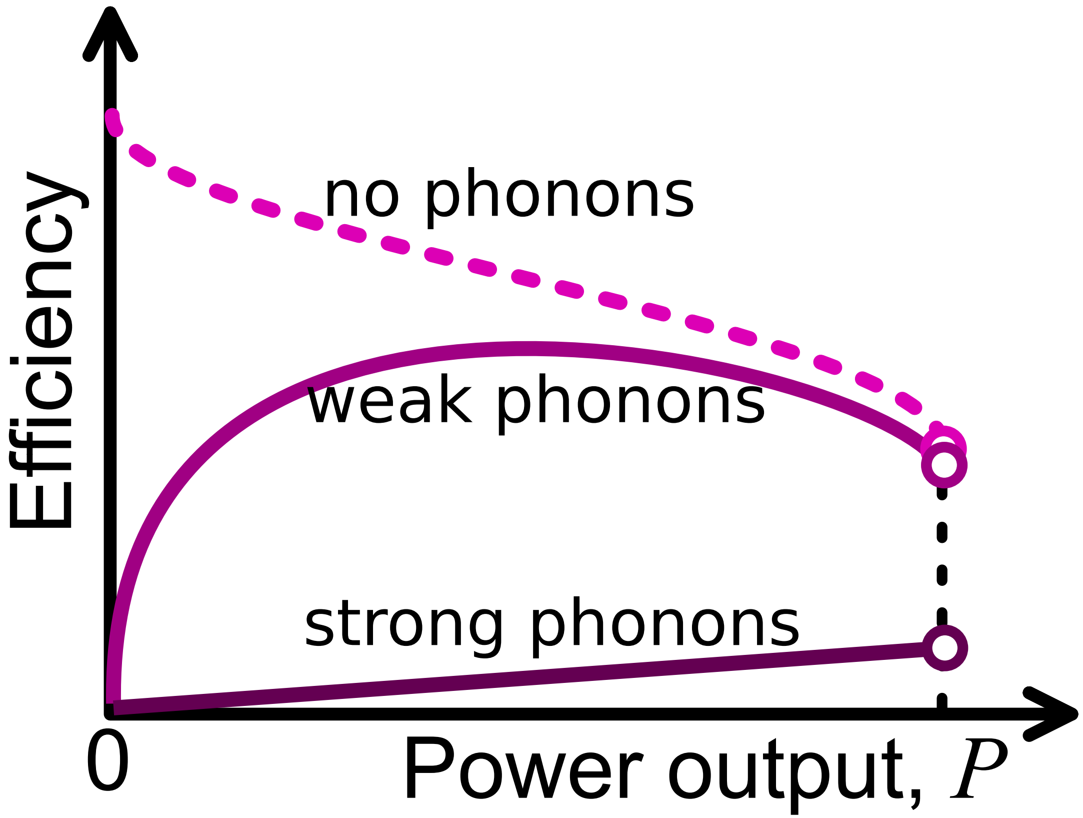
Trade-off between power and efficiency



Result from (nonlinear) scattering theory

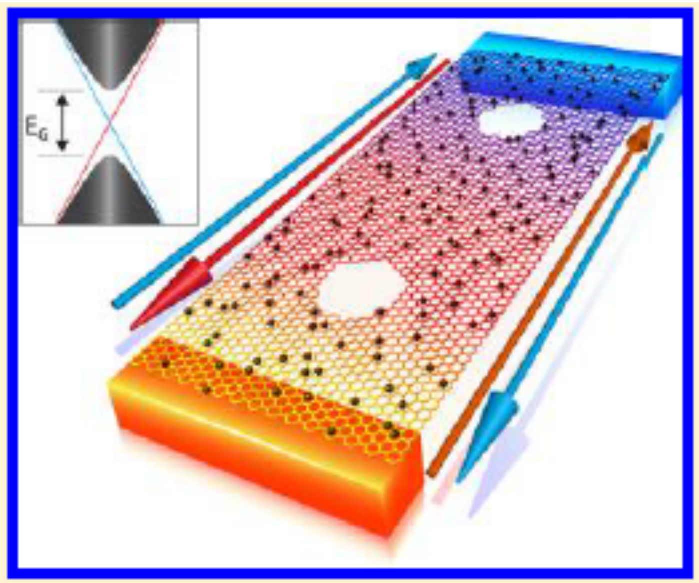
[Whitney, PRL **112**, 130601 (2014); PRB **91**, 115425 (2015)]

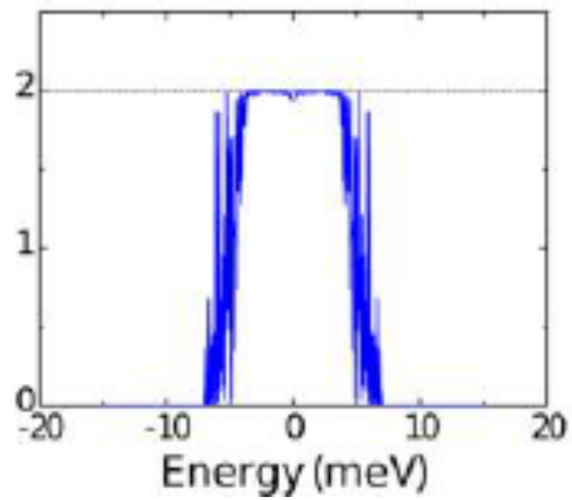
Power-efficiency trade-off including phonons

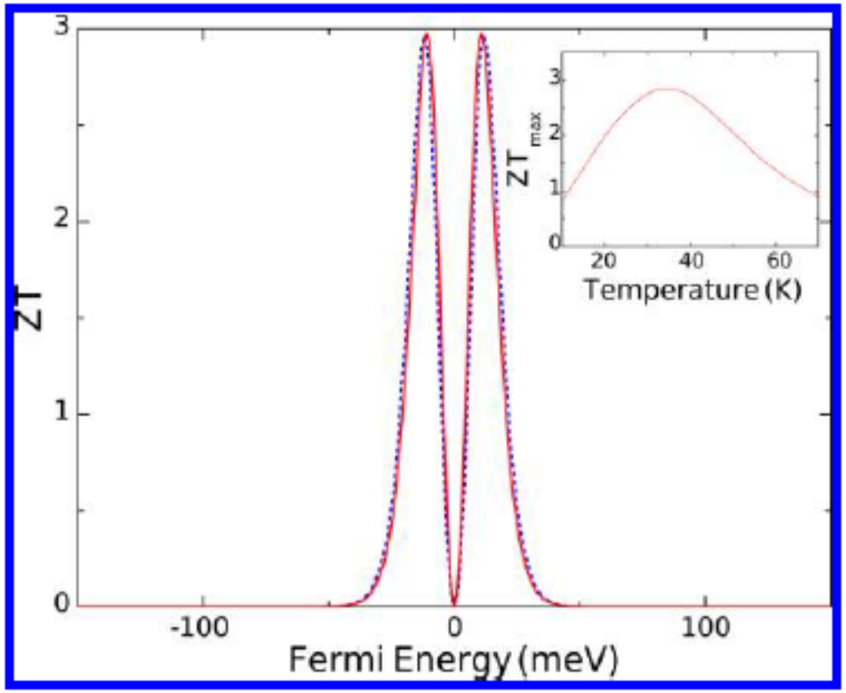


[see Whitney, PRB **91**, 115425 (2015)]

Boxcar transmission in topological insulators





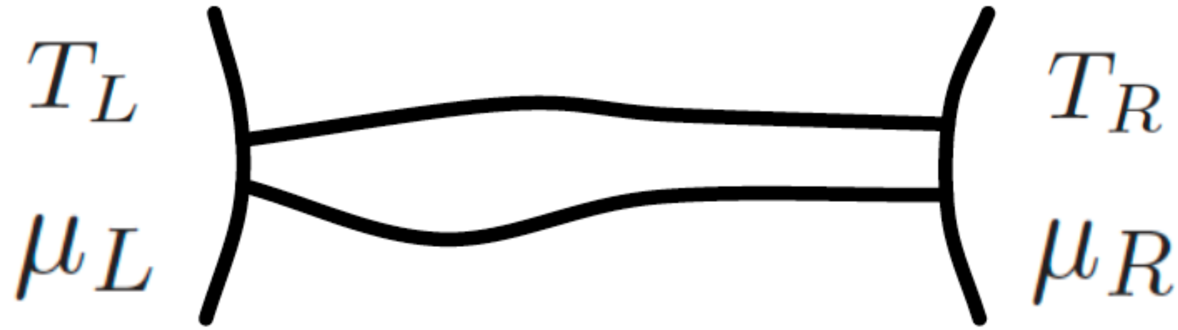


Graphene nanoribbons with heavy adatoms and nanopores

[Chang et al., Nanolett., 14, 3779 (2014)]

Linear response for coupled (particle and heat) flows

Stochastic baths: ideal gases at fixed temperature and electrochemical potential



$$\begin{cases} J_e = L_{ee}\mathcal{F}_e + L_{eh}\mathcal{F}_h \\ J_h = L_{he}\mathcal{F}_e + L_{hh}\mathcal{F}_h \end{cases}$$

Onsager relation (for time-reversal symmetric systems):

$$L_{eh} = L_{he}$$

Positivity of entropy production:

$$L_{ee} \geq 0, \quad L_{hh} \geq 0, \quad \det \boldsymbol{L} \geq 0$$

$$\mathcal{F}_e = \Delta V/T \;\; (\Delta V = \Delta\mu/e)$$

$$\mathcal{F}_h = \Delta T/T^2$$

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

$$\Delta T = T_L - T_R$$

(we assume $T_L > T_R, \;\; \mu_L < \mu_R$)

Onsager and transport coefficients

$$G = \left(\frac{J_e}{\Delta V}\right)_{\Delta T=0} = \frac{L_{ee}}{T}$$

$$K = \left(\frac{J_h}{\Delta T}\right)_{J_e=0} = \frac{1}{T^2}\frac{\det \boldsymbol{L}}{L_{ee}}$$

$$S = -\left(\frac{\Delta V}{\Delta T}\right)_{J_e=0} = \frac{1}{T}\frac{L_{eh}}{L_{ee}}$$

Note that the positivity of entropy production implies that the (isothermal) electric conductance G>0 and the thermal conductance K>0

Seebeck and Peltier coefficients

$$\Pi = \left(\frac{J_h}{J_e}\right)_{\Delta T=0} = \frac{L_{he}}{L_{ee}}$$

$$\Pi(\boldsymbol{B}) = TS(-\boldsymbol{B})$$

Seebeck and Peltier coefficients are related a Onsager reciprocal relation (when time symmetry is not broken, we simply have $\Pi = TS$)

Interpretation of the Peltier coefficient

$$\begin{cases} J_e = G\Delta V + GS\Delta T, \\ \\ J_h = G\Pi\Delta V + (K + GS\Pi)\Delta T \end{cases}$$

Entropy current:

$$J_{\mathscr{S}} = \frac{J_h}{T} = \frac{\Pi}{T} J_e + \frac{K}{T}\Delta T$$

Π/T *entropy transported by the electron flow*

$J_e = eJ_\rho$ each electron carries an entropy of $e\Pi/T$

ΠJ_e *advective* term in thermal transport (reversible)

$K\Delta T$ *open-circuit* term in thermal transport (by electrons and phonons, irreversible)

Entropy production/ heat dissipation rate

$$\dot{\mathscr{S}} = \mathcal{F}_e J_e + \mathcal{F}_h J_h = L_{ee}\mathcal{F}_e^2 + L_{hh}\mathcal{F}_h^2 + (L_{eh} + L_{he})\mathcal{F}_e\mathcal{F}_h$$

$$\dot{Q} = T\dot{\mathscr{S}} = \frac{J_e^2}{G} + \frac{K}{T}(\Delta T)^2 + J_e(\Pi - TS)\frac{\Delta T}{T}$$

Joule heating

heat lost by
thermal resistance

disappears for time-reversal
symmetric systems

To minimize
dissipation large G and
small K are needed

Linear response?

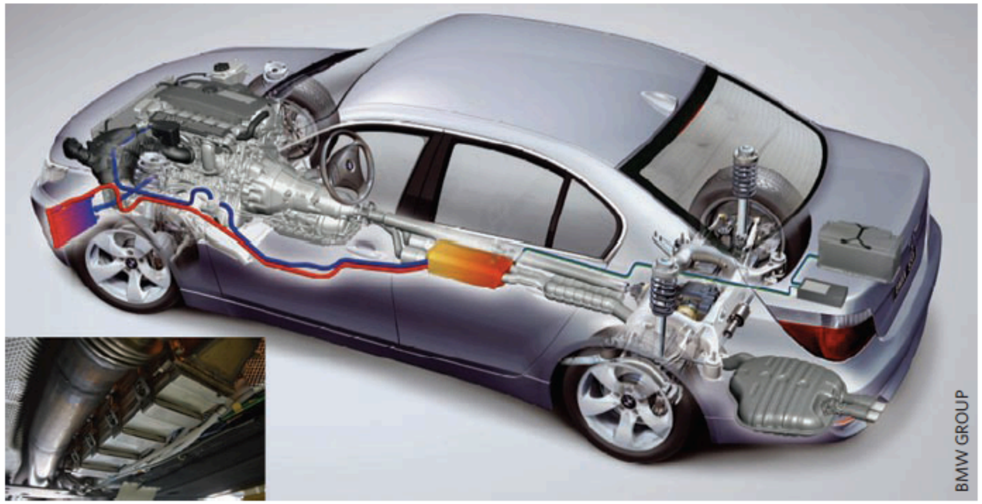


Figure 1 | Integrating thermoelectrics into vehicles for improved fuel efficiency. Shown is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue).

[Vining, Nat. Mater. **8**, 83 (2009)]

$$T_H \sim 600 - 700\,\mathrm{K}$$

(exhaust gases)

$$T_C \sim 270 - 300\,\mathrm{K}$$

(room temperature)

Linear response for small temperature and electrochemical potential differences (compared to the average temperature) on the scale of the relaxation length

Exhaust pipe: temperature drop over a mm scale: temperature drop of 0.003 K on the relaxation length scale (of 10 nm)

Maximum efficiency

Within linear response and for steady-state heat to work conversion:

$$\eta = \frac{P}{\dot{Q}_L} = \frac{-(\Delta V) J_e}{J_h} = \frac{-T \mathfrak{F}_e (L_{ee} \mathfrak{F}_e + L_{eh} \mathfrak{F}_h)}{L_{he} \mathfrak{F}_e + L_{hh} \mathfrak{F}_h}$$

Find the maximum of η over $\mathfrak{F}_e$ for fixed $\mathfrak{F}_h$ i.e., over the applied voltage ΔV for fixed temperature difference ΔT)

Maximum achieved for $\mathfrak{F}_e = \frac{L_{hh}}{L_{he}} \left(-1 + \sqrt{\frac{\det \boldsymbol{L}}{L_{ee} L_{hh}}} \right) \mathfrak{F}_h$

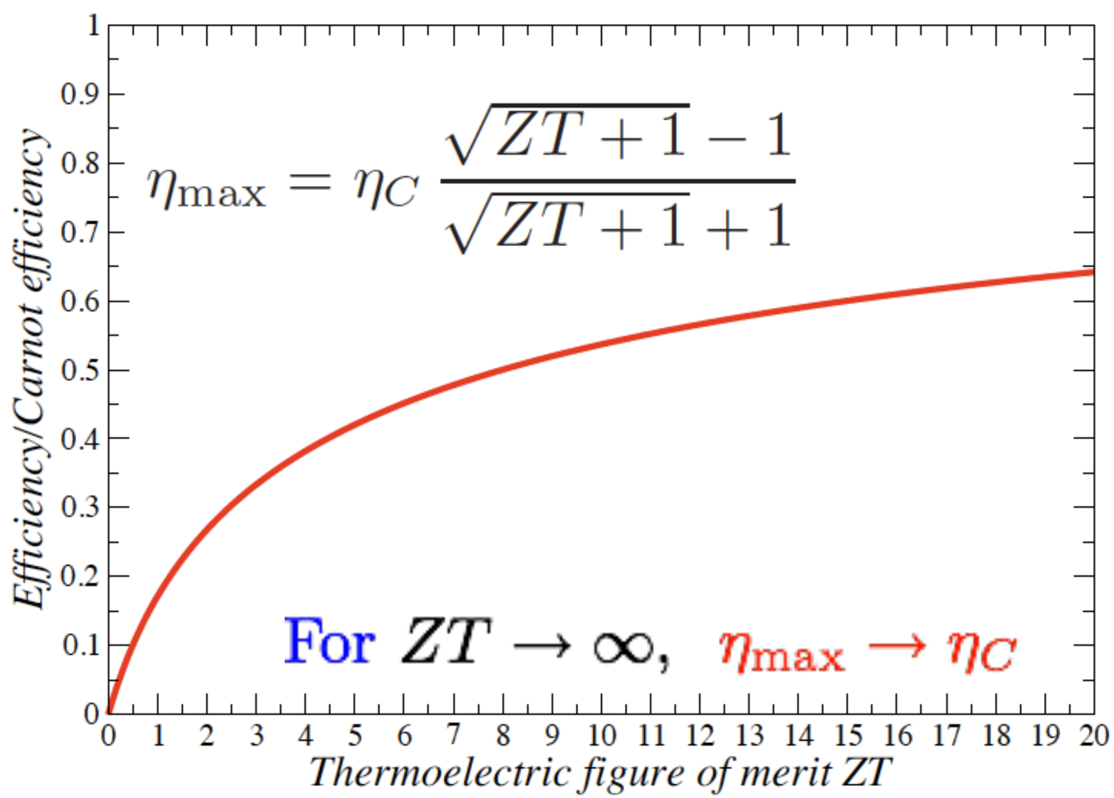
Maximum efficiency (for system with time-reversal symmetry)

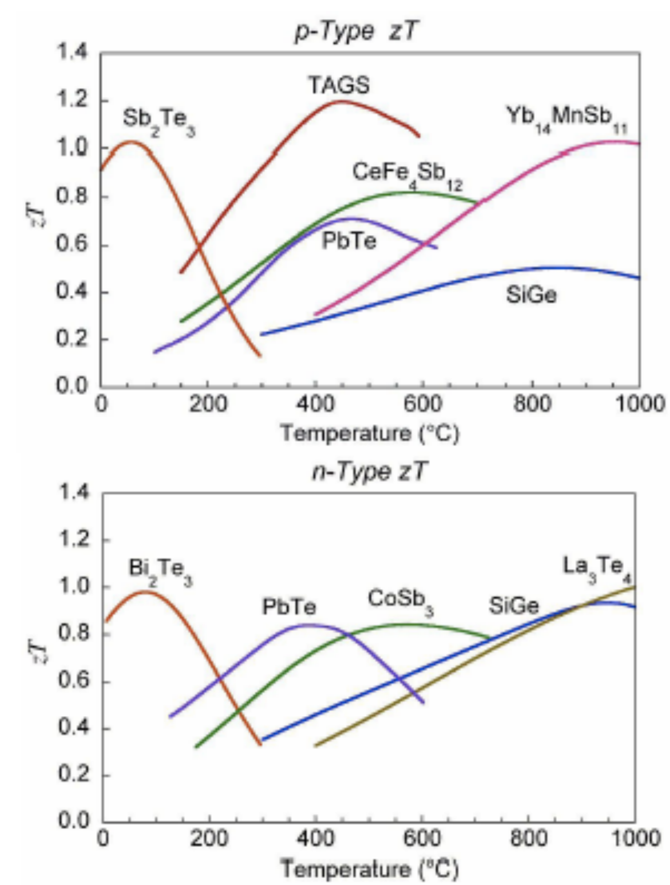
$$\eta_{\max} = \eta_C \frac{\sqrt{ZT+1} - 1}{\sqrt{ZT+1} + 1} \qquad (T_L \approx T_R \approx T)$$

Thermoelectric figure of merit

$$ZT \equiv \frac{L_{eh}^2}{\det \mathbf{L}} = \frac{GS^2}{K}T$$

Positivity of entropy production implies $ZT > 0$





Conditions for Carnot efficiency

ZT **diverging implies that the Onsager matrix is ill-conditioned, that is, the condition number diverges:**

$$\mathrm{cond}(\boldsymbol{L}) \equiv \frac{[\mathrm{Tr}(\boldsymbol{L})]^2}{\det \boldsymbol{L}} > ZT \qquad \begin{cases} J_e = L_{ee}\mathfrak{F}_e + L_{eh}\mathfrak{F}_h \\ \\ J_h = L_{he}\mathfrak{F}_e + L_{hh}\mathfrak{F}_h \end{cases}$$

In such case the system is singular (tight coupling limit):

$$J_h \propto J_e$$

(the ratio J_h/J_e is independent of the applied voltage and temperature gradients)

Efficiency at maximum power

Output power $P = -(\Delta V)J_e = -T\mathfrak{F}_e(L_{ee}\mathfrak{F}_e + L_{eh}\mathfrak{F}_h)$

Find the maximum of P over $\mathfrak{F}_e$ for fixed $\mathfrak{F}_h$ (over the applied voltage ΔV for fixed ΔT)

Maximum achieved for $\mathfrak{F}_e = -\dfrac{L_{eh}}{2L_{ee}}\mathfrak{F}_h$

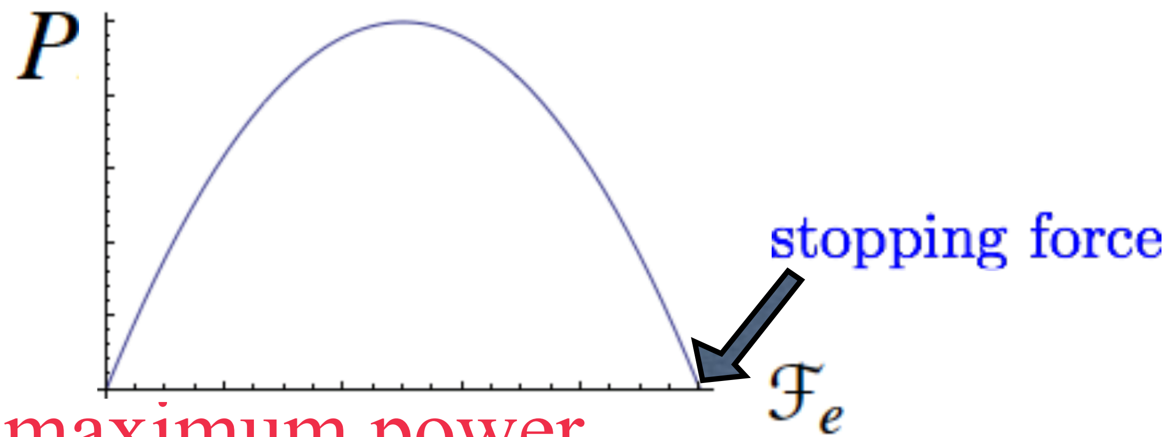
Maximum output power

$$P_{\max} = \frac{T}{4}\frac{L_{eh}^2}{L_{ee}}\mathcal{F}_h^2 = \frac{1}{4}S^2G(\Delta T)^2$$

Power factor S^2G

P quadratic function of $\mathcal{F}_e$, with maximum at half of the *stopping force*:

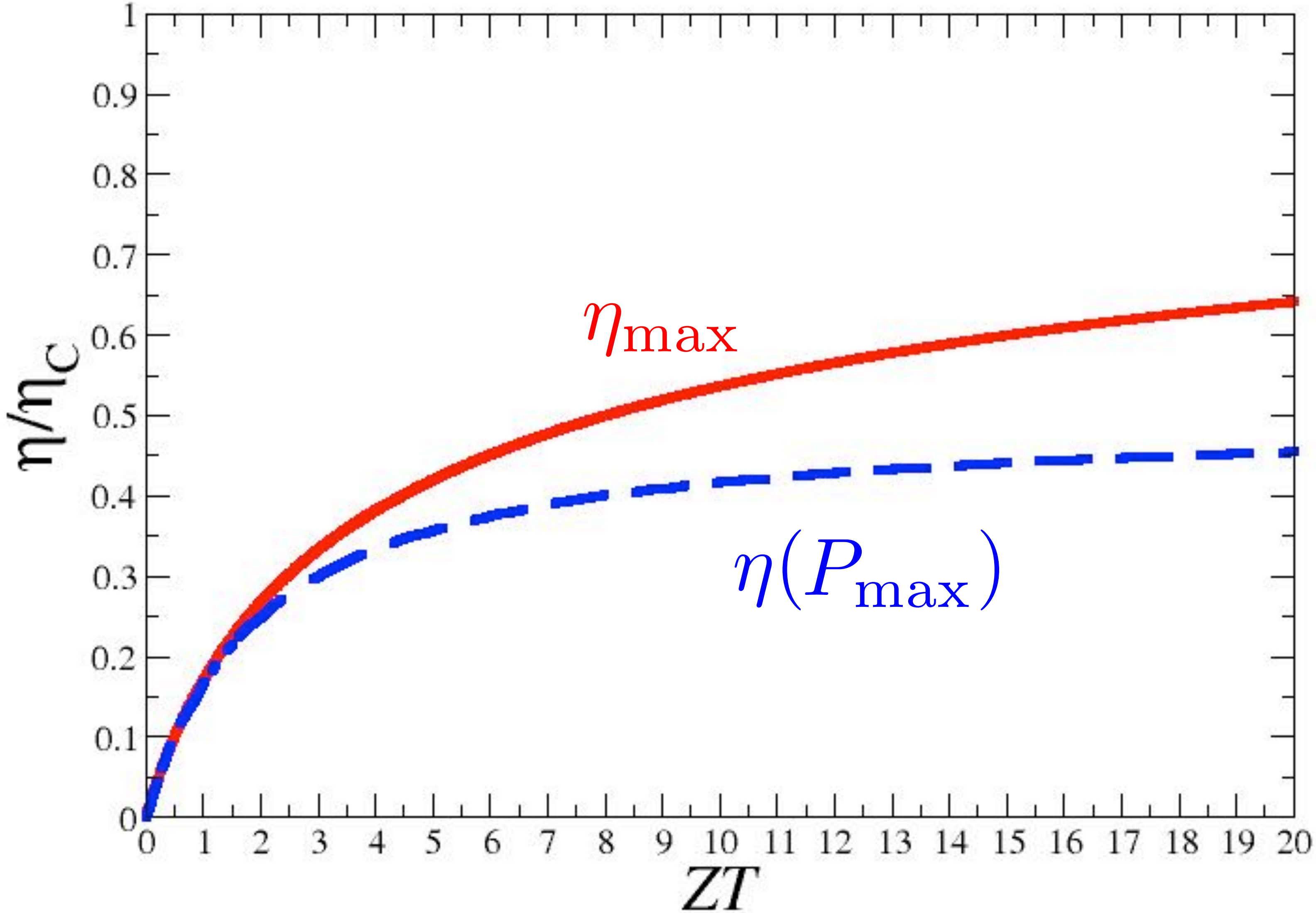
$$\mathcal{F}_e^{\text{stop}} = -\frac{L_{eh}}{L_{ee}}\mathcal{F}_h, \qquad J_e(\mathcal{F}_e^{\text{stop}}) = 0$$



Efficiency at maximum power

$$\eta(P_{\max}) = \frac{\eta_C}{2}\frac{ZT}{ZT+2} \le \eta_{CA} \equiv \frac{\eta_C}{2}$$

η_{CA} Curzon-Ahlborn upper bound

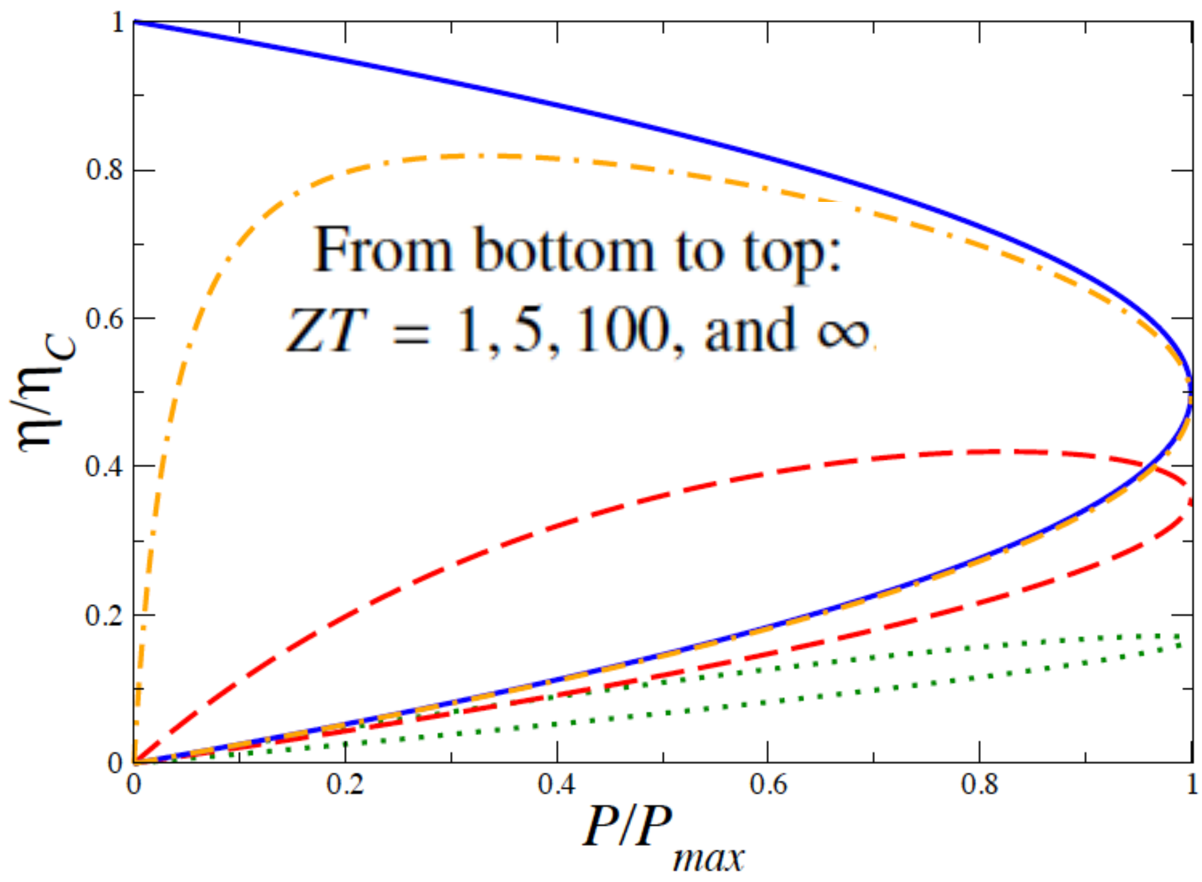


1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
η/η_C
$\eta_{\max}$
$\eta(P_{\max})$
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
ZT

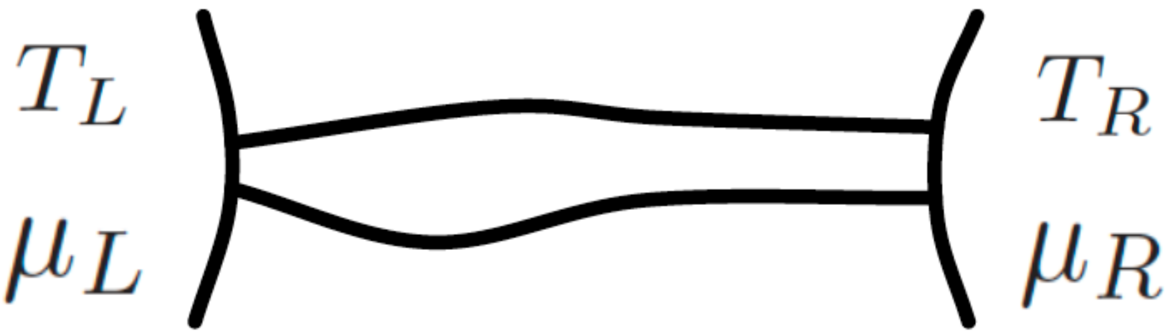
Efficiency versus power

$$r = \mathfrak{F}_e / \mathfrak{F}_e^{\text{stop}} \qquad \frac{P}{P_{\max}} = 4r(1-r) \quad \Longrightarrow \quad r = \frac{1}{2}\left[1 \pm \sqrt{1 - \frac{P}{P_{\max}}}\right]$$

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



Maximum refrigeration efficiency



$(T_L > T_R)$

Cooling power J_h (heat extracted from the cold reservoir)

Coefficient of performance (COP)

$$\eta^{(r)} = \frac{J_h}{P} \qquad (J_h < 0,\ P < 0)$$

$$\eta^{(r)}_{\max} = \eta^{(r)}_C \frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+1}, \qquad \eta^{(r)}_C = T_R/(T_L - T_R)$$

(can be >1)

ZT is the figure of merit also for refrigeration

ZT is an intrinsic material property?

For mesoscopic systems size-dependence for G,K,S can be expected

In the diffusive transport regime Ohm's and Fourier's scaling laws hold:

$$G = \sigma A/\Lambda \qquad\qquad A \text{ cross section area}$$

$$K = \kappa A/\Lambda \qquad\qquad \Lambda \text{ length of the material}$$

$$G/K = \sigma/\kappa \quad \Rightarrow \quad ZT = \frac{\sigma S^2}{\kappa} T$$

Local equilibrium

Under the assumption of local equilibrium we can write phenomenological equations with ∇T and ∇μ rather than ΔT and Δμ

$$\begin{cases} j_e = \lambda_{ee}(-\nabla\mu/eT) + \lambda_{eh}\nabla(1/T) \\ \\ j_h = \lambda_{he}(-\nabla\mu/eT) + \lambda_{hh}\nabla(1/T) \end{cases}$$

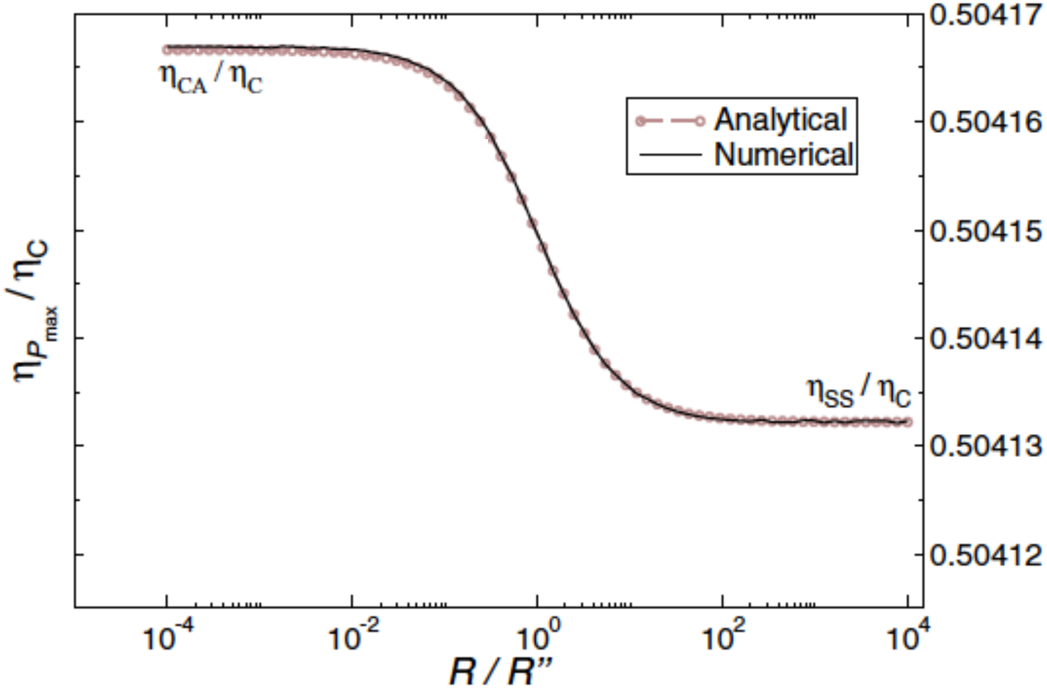
j_e, j_h charge and heat current densities

In this case we connect Onsager coefficients to electric and thermal conductivity rather than to conductances

$$\sigma = \left(\frac{j_e}{\nabla V}\right)_{\nabla T=0}, \quad \kappa = \left(\frac{j_h}{\nabla T}\right)_{j_e=0}$$

Crossover from endoreversible to exoreversible regimes

Thermoelectric generator: internal dissipation (Joule heating, thermal conductance) and external dissipation (dissipative thermal coupling to reservoirs)



[Apertet, Ouerdane, Goupil, Lecoeur, PRE 85, 031116 (2012)]

Linear response and Landauer formalism

The Onsager coefficients are obtained from the linear response expansion of the charge and thermal currents

$$f_L(E) \approx f(E) + \frac{\partial f}{\partial T}\Delta T + \frac{\partial f}{\partial \mu}\Delta\mu = f(E) - \frac{\partial f}{\partial E}\left[(E-\mu)\frac{\Delta T}{T} + \Delta\mu\right]$$

$$-\frac{\partial f}{\partial E} = \frac{1}{4k_B T\cosh^2[(E-\mu)/2k_B T]}$$

$$L_{ee} = e^2 T I_0, \quad L_{eh} = L_{he} = eTI_1, \quad L_{hh} = TI_2$$

$$I_n = \frac{1}{h}\int_{-\infty}^{\infty} dE(E-\mu)^n \tau(E)\left(-\frac{\partial f}{\partial E}\right)$$

Wiedemann-Franz law

Phenomenological law: the ratio of the thermal to the electrical conductivity is directly proportional to the temperature, with a universal proportionality factor.

$$\frac{\kappa}{\sigma} = \mathfrak{L} T$$

Lorenz number

$$\mathfrak{L} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$$

Sommerfeld expansion

The Wiedemann-Franz law can be derived for low-temperature non-interacting systems both within kinetic theory or Landauer approach

In both cases it is substantiated by Sommerfeld expansion. Within Landauer approach we consider

$$J_{\mathrm{h,L}} = \frac{1}{h}\int_{-\infty}^{\infty} dE(E-\mu_{\mathrm{L}})\tau(E)[f_L(E)-f_R(E)]$$

$$J_e = eJ_\rho = \frac{e}{h}\int_{-\infty}^{\infty} dE\tau(E)[f_L(E)-f_R(E)]$$

We assume smooth transmission functions $\tau(E)$ in the neighborhood of $E=\mu$:

$$\tau(E) \approx \tau(\mu) + \left.\frac{d\tau(E)}{dE}\right|_{E=\mu}(E-\mu)$$

To leading order in $k_B T/E_F$ with $E_F = \mu(T = 0)$

$$I_0 \approx \frac{\tau(\mu)}{h}, \quad I_1 \approx \frac{\pi^2}{3h}(k_B T)^2 \left.\frac{d\tau(E)}{dE}\right|_{E=\mu}, \quad I_2 \approx \frac{\pi^2}{3h}(k_B T)^2 \tau(\mu)$$

$$G = e^2 I_0 \approx \frac{e^2}{h}\tau(\mu), \quad K = \frac{1}{T}\left(I_2 - \frac{I_1^2}{I_0}\right) \approx \frac{\pi^2 k_B^2 T}{3h}\tau(\mu)$$

Neglected I_1^2/I_0 with respect to I_2, which in turn implies $L_{ee}L_{hh} >> (L_{eh})^2$ and $K \approx L_{hh}/T^2$

Wiedemann-Franz law:

$$\frac{K}{G} \approx \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

Wiedemann-Franz law and thermoelectric efficiency

$$ZT = \frac{GS^2}{K} T = \frac{S^2}{\mathfrak{L}}$$

Wiedemann-Franz law derived under the condition $L_{ee}L_{hh} >> (L_{eh})^2$ and therefore

$$ZT = L_{eh}^2 / \det \boldsymbol{L} \approx L_{eh}^2 / L_{ee} L_{hh} \ll 1$$

Wiedemann-Franz law violated in
- low-dimensional interacting systems that exhibit non-Fermi liquid behavior
- (smll) systems where transmission can show significant energy dependence

(Violation of) Wiedemann-Franz law in small systems

Consider a (basic) model of a molecular wire coupled to electrodes:

$$H = H_W + H_E + H_{WE},$$

$$H_W = -t \sum_{i=1}^{N-1} (c_i^\dagger c_{i+1} + \text{h.c.}),$$

$$H_E = \sum_{j=L,R} \sum_k E_{kj} d_{kj}^\dagger d_{kj},$$

$$H_{WE} = \sum_k (t_{kL} c_1^\dagger d_{kL} + t_{kR} c_N^\dagger d_{kR} + \text{h.c.})$$

Transmission: $\tau(E) = \mathrm{Tr}(\Gamma_L(E) G_s^\dagger(E) \Gamma_R(E) G_s(E))$

Green's function: $G_s(E) = (E - H_W - \Sigma_L - \Sigma_R)^{-1}$

Level broadening functions: $\Gamma_{L,R}(E) = i[\Sigma_{L,R}(E) - \Sigma_{L,R}^\dagger(E)]$

Self-energies: $\Sigma_{L,R}(E)$

Wide band limit: level widths energy independent:

$$\gamma_j = 2\pi \sum_k |t_{kj}|^2 \delta(E - E_{kj})$$

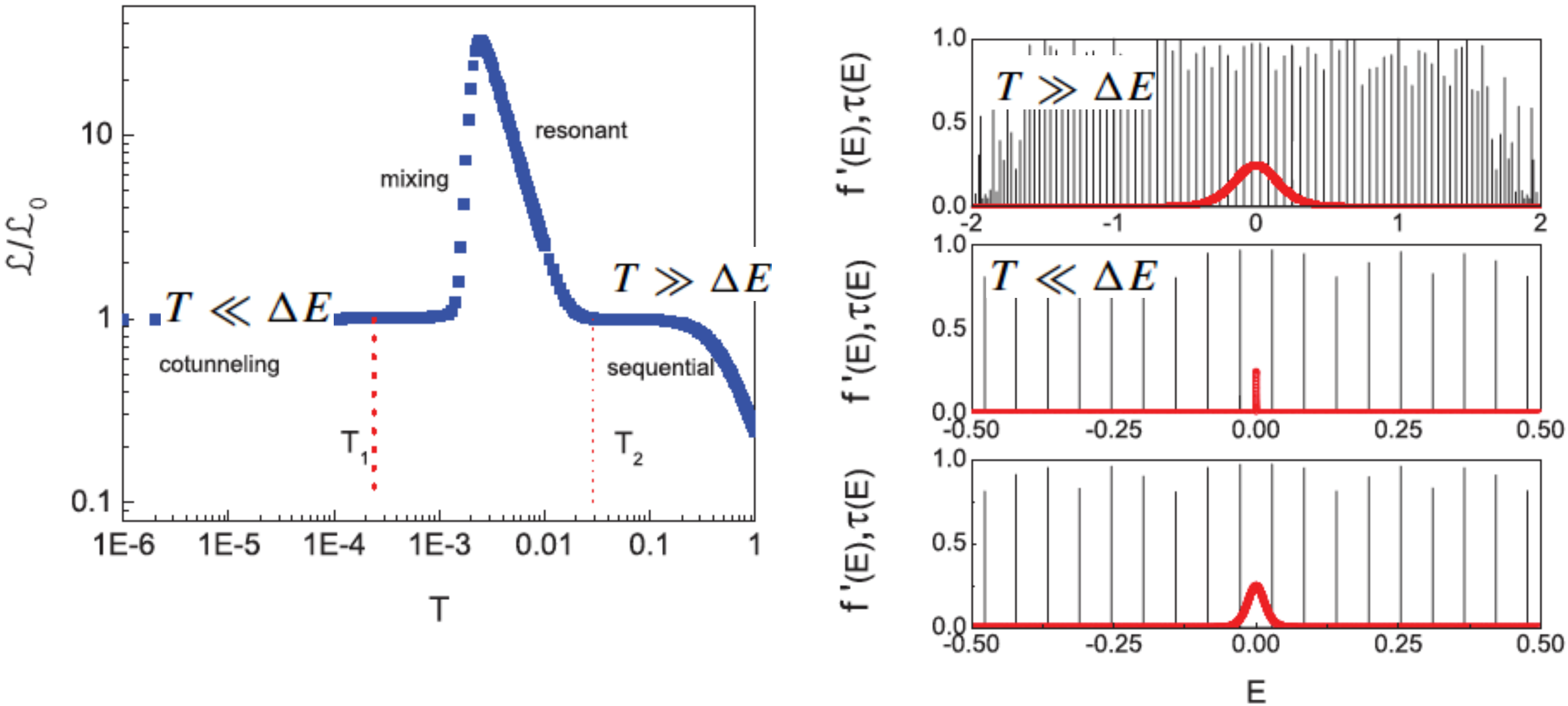
Take $\gamma_L = \gamma_R = \gamma$

$$\Gamma_L = \gamma c_1^\dagger c_1, \Gamma_R = \gamma c_N^\dagger c_N$$

Transmission: $\tau(E) = \gamma^2 |\langle 1|G_s(E)|N\rangle|^2$

Green's function obtained by inverting

$$\begin{pmatrix} E - i\frac{\gamma}{2} & -1 & . & . & . \\ -1 & E & . & . & . \\ 0 & . & . & . & . \\ . & . & . & E & -1 \\ . & . & . & -1 & E + i\frac{\gamma}{2} \end{pmatrix}$$



(Bosisio, Balachandran, Benenti, PRB **86**, 035433 (2012);
see also Vavilov and Stone, PRB **72**, 205107 (2005))

Mott's formula for thermopower

For non-interacting electrons (thermopower vanishes when there is particle-hole symmetry)

$$S = \frac{1}{eT}\frac{I_1}{I_0} = \frac{1}{eT}\frac{\int_{-\infty}^{\infty} dE(E-\mu)\tau(E)\left(-\frac{\partial f}{\partial E}\right)}{\int_{-\infty}^{\infty} dE\tau(E)\left(-\frac{\partial f}{\partial E}\right)} = \frac{1}{eT}\langle E-\mu\rangle$$

Consider smooth transmissions $\tau(E) \approx \tau(\mu) + \tau'(\mu)(E-\mu)$

$$S \approx \frac{\pi^2 k_B^2 T}{3e}\frac{\tau'(\mu)}{\tau(\mu)} = \frac{\pi^2 k_B^2 T}{3e}\left.\frac{d\ln G(E)}{dE}\right|_{E=\mu}$$

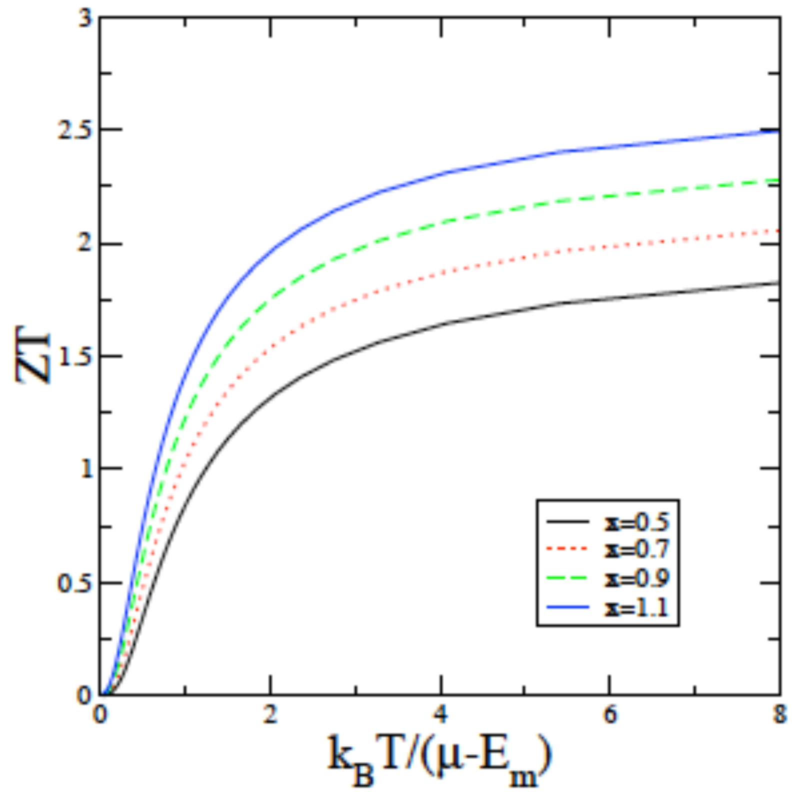
Electron and holes contribute with opposite signs: we want sharp, asymmetric transmission functions to have large *S* (ex: resonances, Anderson QPT, see Imry and Amir, 2010), violation of WF, possibly large ZT.

Metal-insulator 3D Anderson transition

$$\sigma = \int_{-\infty}^{\infty} dE \sigma_0(E) \left(-\frac{\partial f}{\partial E} \right) \qquad \sigma_0(E) = \begin{cases} A(E - E_m)^x, & \text{if } E \geq E_m, \\ 0, & \text{if } E \leq E_m, \end{cases}$$

x conductivity critical exponent

[G.B., H. Ouerdane, C. Goupil, arXiv:1602.06590; Comptes Rendus Physique, in press]



Energy filtering

$$\frac{K}{G} = \frac{\langle (E-\mu)^2 \rangle - \langle E-\mu \rangle^2}{e^2 T}$$

For good thermoelectric we desire violation of WF law such that:

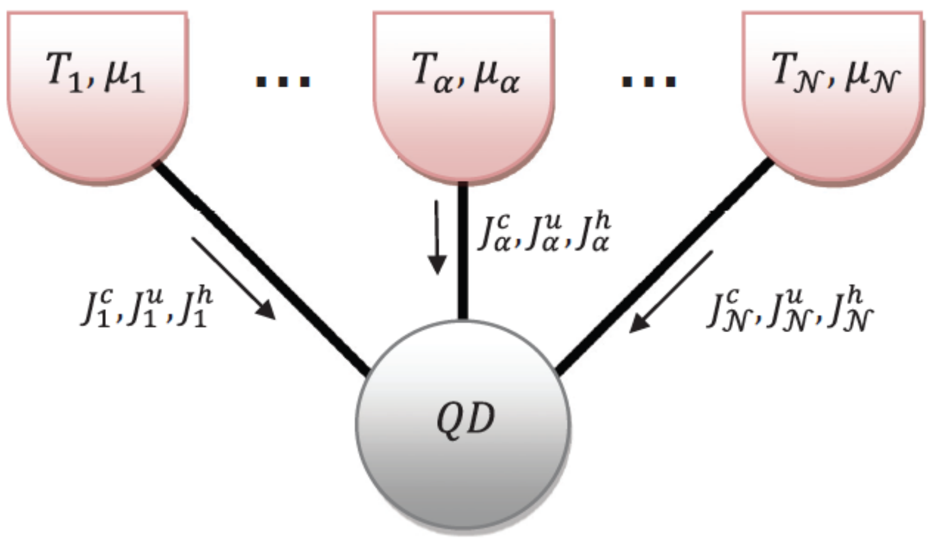
$$K/G \to 0$$

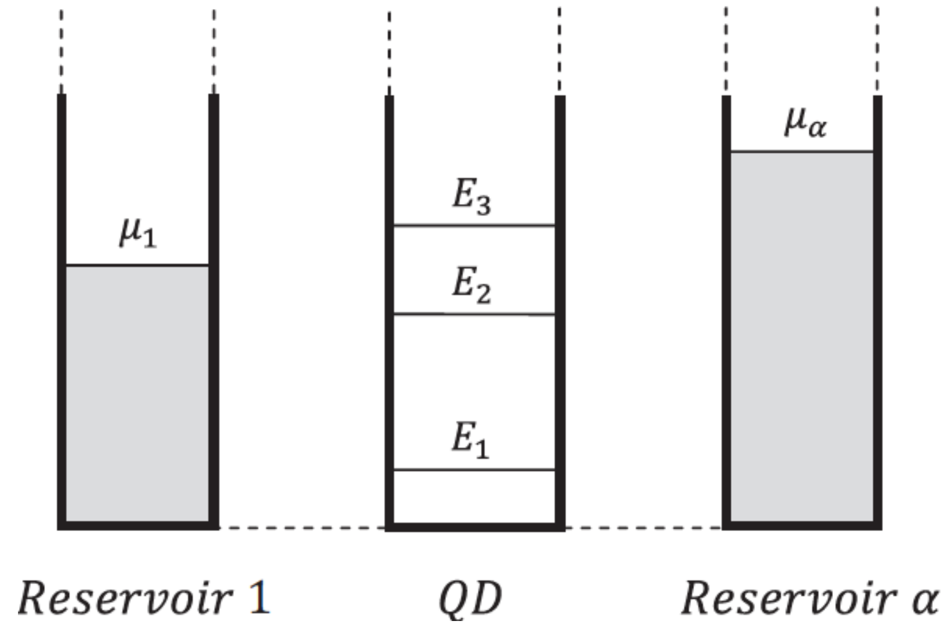
$$ZT = \frac{\langle (E-\mu) \rangle^2}{\langle (E-\mu)^2 \rangle - \langle (E-\mu) \rangle^2}$$

No dispersion with delta-energy filtering: ZT diverges

Thermoelectricity in the Coulomb blockade regime, Kinetic equations. Quantum dot model

Multilevel interacting quantum dot





Discrete energy levels: ideal to implement energy filtering

Study the effects of Coulomb interaction between electrons

[Erdmann, Mazza, Bosisio, G.B., Fazio, Taddei PRB **95**, 245432 (2017)]

Sequential (single-electron) tunnelling regime

E_p (with $p = 1, 2, \ldots$) single-electron levels of the QC

C capacitance

N number of electrons in the dot

$(Ne)^2/2C$ electrostatic (Coulomb) interaction

$\Gamma_\alpha(p)$ tunneling rate from level p to reservoir α

Weak coupling to the reservoirs: thermal energy $k_B T$, level spacing and charging energy much larger than the coupling energy $\hbar \sum_\alpha \Gamma_\alpha(p)$ between the QD and the reservoirs: charge quantized $n_p = 0$ or $n_p = 1$ $N = \sum_i n_i$

Electrostatic energy $U(N) = E_C N^2$,

single-electron charging energy $E_C = e^2/2C$

Energy conservation

Configuration determined by occupation numbers $\{n_i\}$

Non-equilibrium probability $P(\{n_i\})$

Energy conservation for tunnelling into or from reservoirs:

$$E_p + U(N) = E^{\text{fin}}(N) + U(N-1)$$

$$E^{\text{in}}(N) + U(N) = E_p + U(N+1)$$

Kinetic equations

One kinetic equation for each configuration:

$$\frac{\partial}{\partial t} P(\{n_i\}) = -\sum_{p\alpha} \delta_{n_p,0} P(\{n_i\}) \Gamma_\alpha(p) f_\alpha\left(E^{\text{in}}(N)\right)$$

$$-\sum_{p\alpha} \delta_{n_p,1} P(\{n_i\}) \Gamma_\alpha(p) \left[1 - f_\alpha\left(E^{\text{fin}}(N)\right)\right]$$

$$+\sum_{p\alpha} \delta_{n_p,0} P(\{n_i\}, n_p = 1) \Gamma_\alpha(p) \left[1 - f_\alpha\left(E^{\text{fin}}(N+1)\right)\right]$$

$$+\sum_{p\alpha} \delta_{n_p,1} P(\{n_i\}, n_p = 0) \Gamma_\alpha(p) f_\alpha\left(E^{\text{in}}(N-1)\right),$$

$$P(\{n_i\}, n_p = 1) = P(\{n_1, \ldots, n_{p-1}, 1, n_{p+1}, \ldots\})$$

$$P(\{n_i\}, n_p = 0) = P(\{n_1, \ldots, n_{p-1}, 0, n_{p+1}, \ldots\})$$

Stationary solution: $\partial P/\partial t = 0, \ \sum_{\{n_i\}} P(\{n_i\}) = 1$

Steady-state currents

Charge current:

$$J_{e,\alpha} = e\sum_{p=1}^{\infty}\sum_{\{n_i\}} P(\{n_i\})\Gamma_\alpha(p)\Big\{\delta_{n_p,0} f_\alpha(E^{\text{in}}(N)) - \delta_{n_p,1}[1 - f_\alpha(E^{\text{fin}}(N))]\Big\}$$

Energy current:

$$J_{u,\alpha} = \sum_{p=1}^{\infty}\sum_{\{n_i\}} P(\{n_i\})\Gamma_\alpha(p)\Big\{\delta_{n_p,0} f_\alpha(E^{\text{in}}(N))E^{\text{in}}(N) \\ -\delta_{n_p,1}[1 - f_\alpha(E^{\text{fin}}(N))]E^{\text{fin}}(N)\Big\}$$

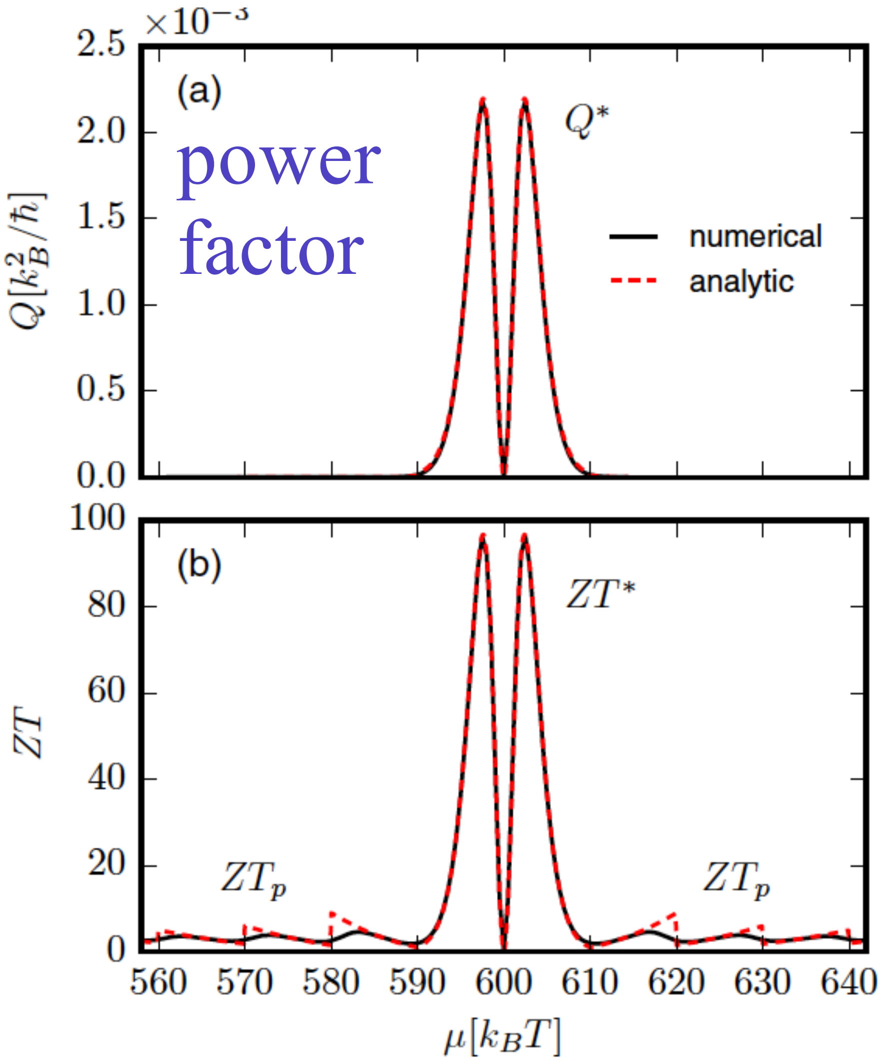
Heat current:

$$J_{h,\alpha} = J_{u,\alpha} - (\mu_\alpha/e)J_{e,\alpha}$$

Quantum limit

Energy spacing and charging energy much bigger than $k_B T$

Analytical results for equidistant levels: $E_p - E_{p-1} = \Delta E$



$$E_C = 50\, k_B T, \quad \Delta E = 10\, k_B T,$$

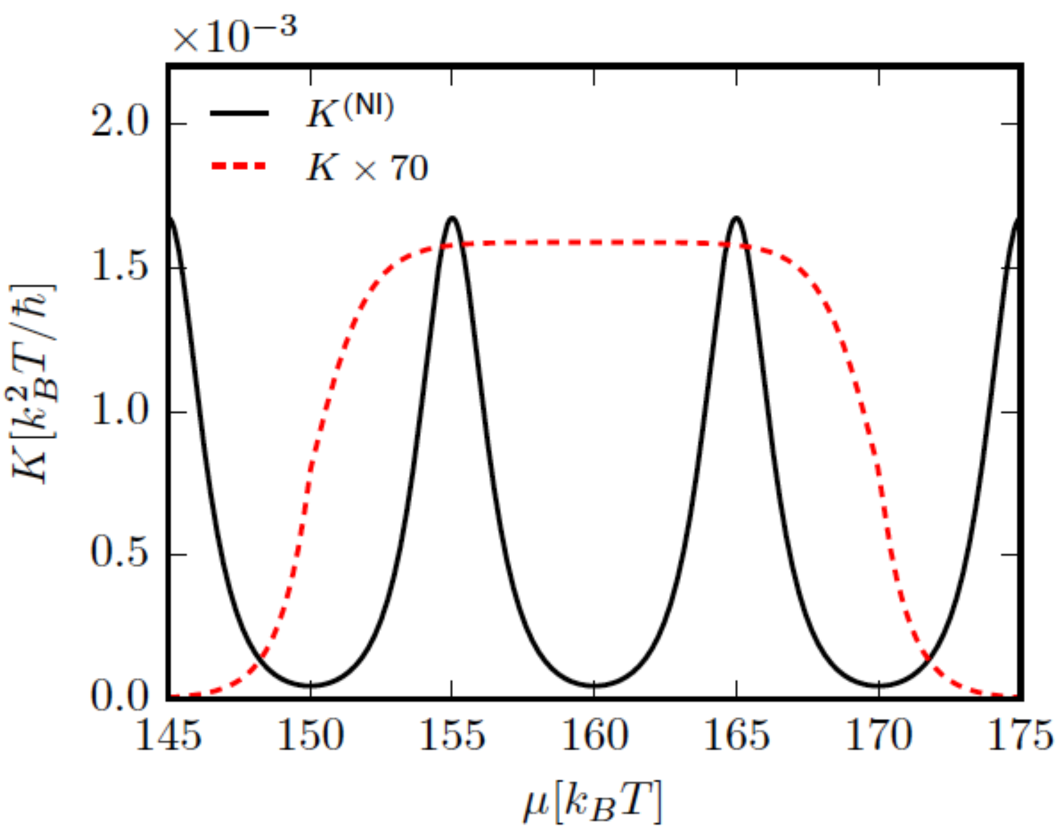
$$\hbar\Gamma_1(p) = \hbar\Gamma_2(p) = (1/100)\, k_B T$$

$$ZT^* \approx 0.44 \frac{e^{\Delta E/k_B T}}{(\Delta E/k_B T)^2}$$

(energy filtering)

Coulomb interaction may enhance the thermoelectric performance of a QD

Compare interacting and non-interacting two-terminal QD with the same energy spacing



Thermal conductance suppressed by Coulomb interaction: ZT is greatly increased.

For a single level K=0 (charge and heat current proportional). For at least two levels Coulomb blockade prevents a second electron to enter when one is already there (electrostatic energy to be paid).

Strongly interacting systems,
Electronic Phase transitions,
Power-efficiency trade-off,
Power-efficiency-fluctuations trade-off,
Carnot efficiency at finite power?
Generality of Onsager reciprocal relations

Short intermezzo: a reason why interactions might be interesting for thermoelectricity

$$K' \equiv \left(\frac{J_h}{\Delta T} \right)_{\Delta V = 0}$$ thermal conductance at zero voltage

$$ZT = \gamma_K - 1, \quad \gamma_K \equiv \frac{K'}{K}$$

If the ratio K'/K diverges, then the Carnot efficiency is achieved

Thermodynamic properties of the working fluid

$$dN = \left.\frac{\partial N}{\partial \mu}\right|_T d\mu + \left.\frac{\partial N}{\partial T}\right|_\mu dT,$$

$$d\mathscr{S} = -\frac{\mu}{T}\,dN + \frac{dU}{T} = -\frac{\mu}{T}\left(\left.\frac{\partial N}{\partial \mu}\right|_T d\mu + \left.\frac{\partial N}{\partial T}\right|_\mu dT\right) + \frac{1}{T}\left(\left.\frac{\partial U}{\partial N}\right|_T dN + \left.\frac{\partial U}{\partial T}\right|_N dT\right)$$

coupled equations:

$$C_{NN} = \left.\frac{\partial N}{\partial \mu}\right|_T, \quad C_{N\mathscr{S}} = \left.\frac{\partial N}{\partial T}\right|_\mu,$$

$$\begin{cases} dN = C_{NN}\,d\mu + C_{N\mathscr{S}}\,dT, \\ d\mathscr{S} = C_{\mathscr{S}N}\,d\mu + C_{\mathscr{S}\mathscr{S}}\,dT, \end{cases}$$

$$C_{\mathscr{S}N} = \frac{1}{T}\left.\frac{\partial N}{\partial \mu}\right|_T\left(\left.\frac{\partial U}{\partial N}\right|_T - \mu\right),$$

capacity matrix $\mathbf{C}$

$$C_{\mathscr{S}\mathscr{S}} = \frac{1}{T}\left[\left.\frac{\partial U}{\partial T}\right|_N + \left.\frac{\partial N}{\partial T}\right|_\mu\left(\left.\frac{\partial U}{\partial N}\right|_T - \mu\right)\right]$$

$$C_{N\mathscr{S}} = C_{\mathscr{S}N}$$

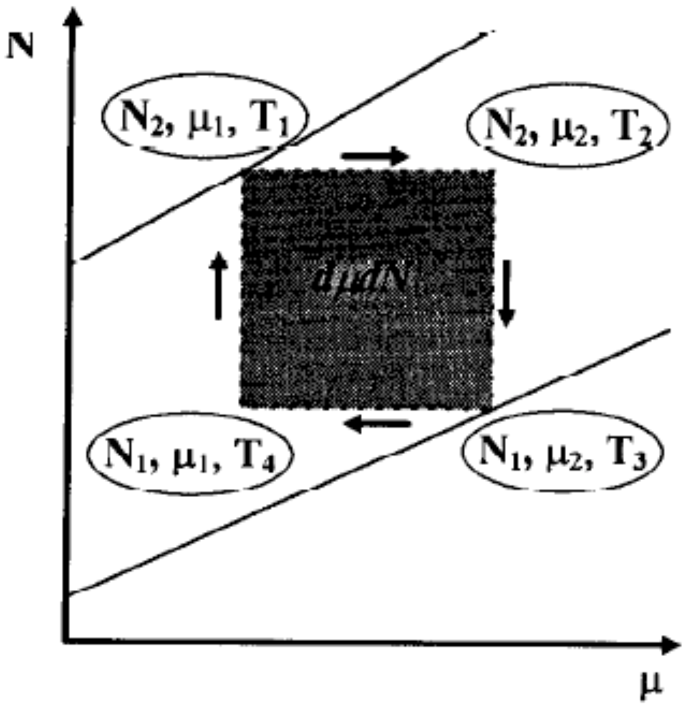
(Vining, MRS Symp. **478**, 3 (1997))

$$C_{\mathscr{S}\mathscr{S}} = \left(\frac{\partial \mathscr{S}}{\partial T}\right)_{\mu} \equiv C_{\mu} \qquad \text{entropy capacity at constant } \mu$$

Setting dN=0 in the coupled equations:

$$C_N \equiv \left(\frac{\partial \mathscr{S}}{\partial T}\right)_N = \frac{\det \boldsymbol{C}}{C_{NN}} \qquad \text{entropy capacity at constant } N$$

Thermodynamic cycle



$$\frac{\eta}{\eta_C} = \frac{-d\mu dN}{d\mathscr{S}dT}$$

$$\eta = \frac{-d\mu dN}{Td\mathscr{S}} = \frac{-d\mu(C_{NN}d\mu + C_{N\mathscr{S}}dT)}{T(C_{\mathscr{S}N}d\mu + C_{\mathscr{S}\mathscr{S}}dT)}$$

maximum efficiency
(over dμ at fixed dT):

$$\eta_{\max} = \eta_C \frac{\sqrt{Z_{\text{th}}T+1}-1}{\sqrt{Z_{\text{th}}T+1}+1}$$

thermodynamic figure of merit:

$$Z_{\text{th}}T = \frac{C_{N\mathscr{S}}^2}{\det \mathbf{C}} = \gamma_{\mu N} - 1, \quad \gamma_{\mu N} \equiv \frac{C_\mu}{C_N}$$

Analogy with a classical gas

$$N \to V, \quad \mu \to -p$$

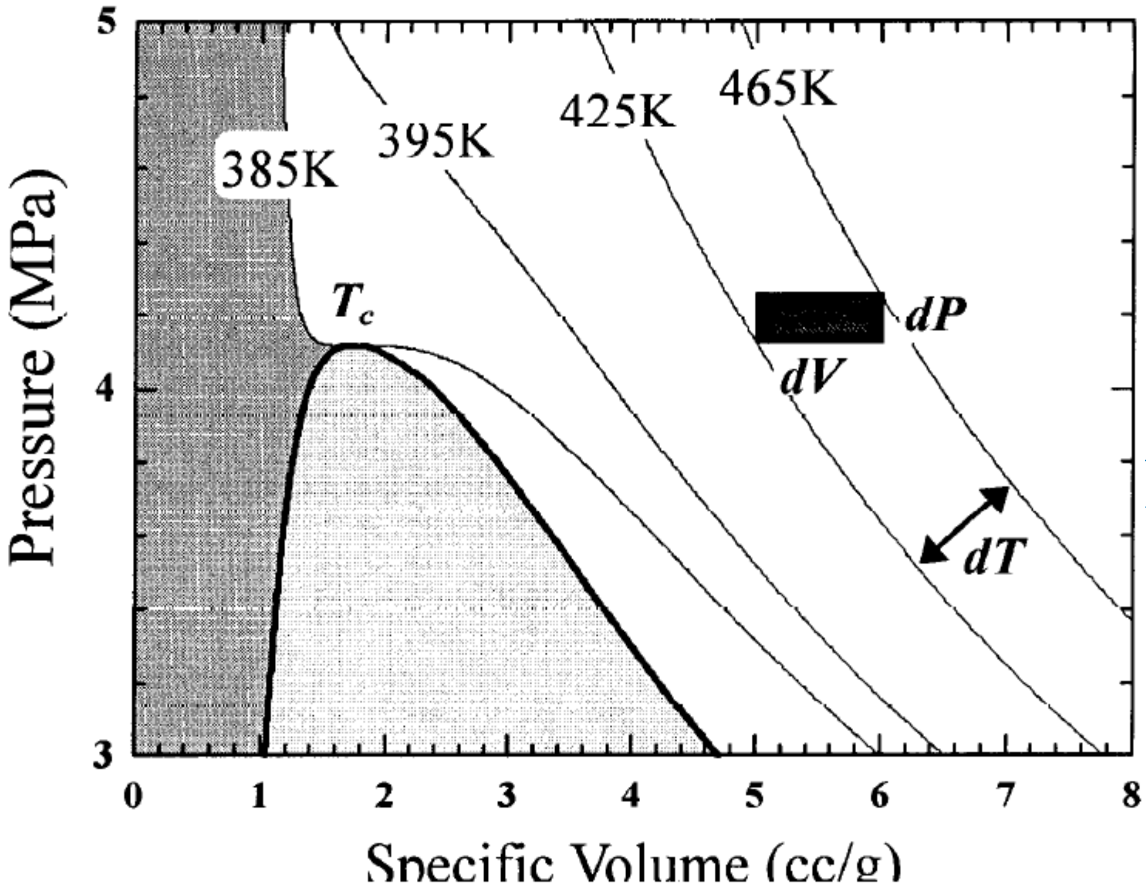


Fig. 5: ***PV*** **diagram for Freon-12 (CCl_2F_2). The two phase region is light gray and the liquid is the darker gray region to the left. Isotherms are indicated by light lines and a typical** ***dPdV*** **element is indicated by the rectangle.**

$$\frac{\eta}{\eta_C} = \frac{dpdV}{dSdT}$$

$$1 + Z_{\mathrm{th}} T = \frac{c_p}{c_V}$$

heat capacity at constant p or V

$$C_p \equiv T \left(\frac{\partial \mathscr{S}}{\partial T} \right)_p ,$$

$$C_V \equiv T \left(\frac{\partial \mathscr{S}}{\partial T} \right)_V$$

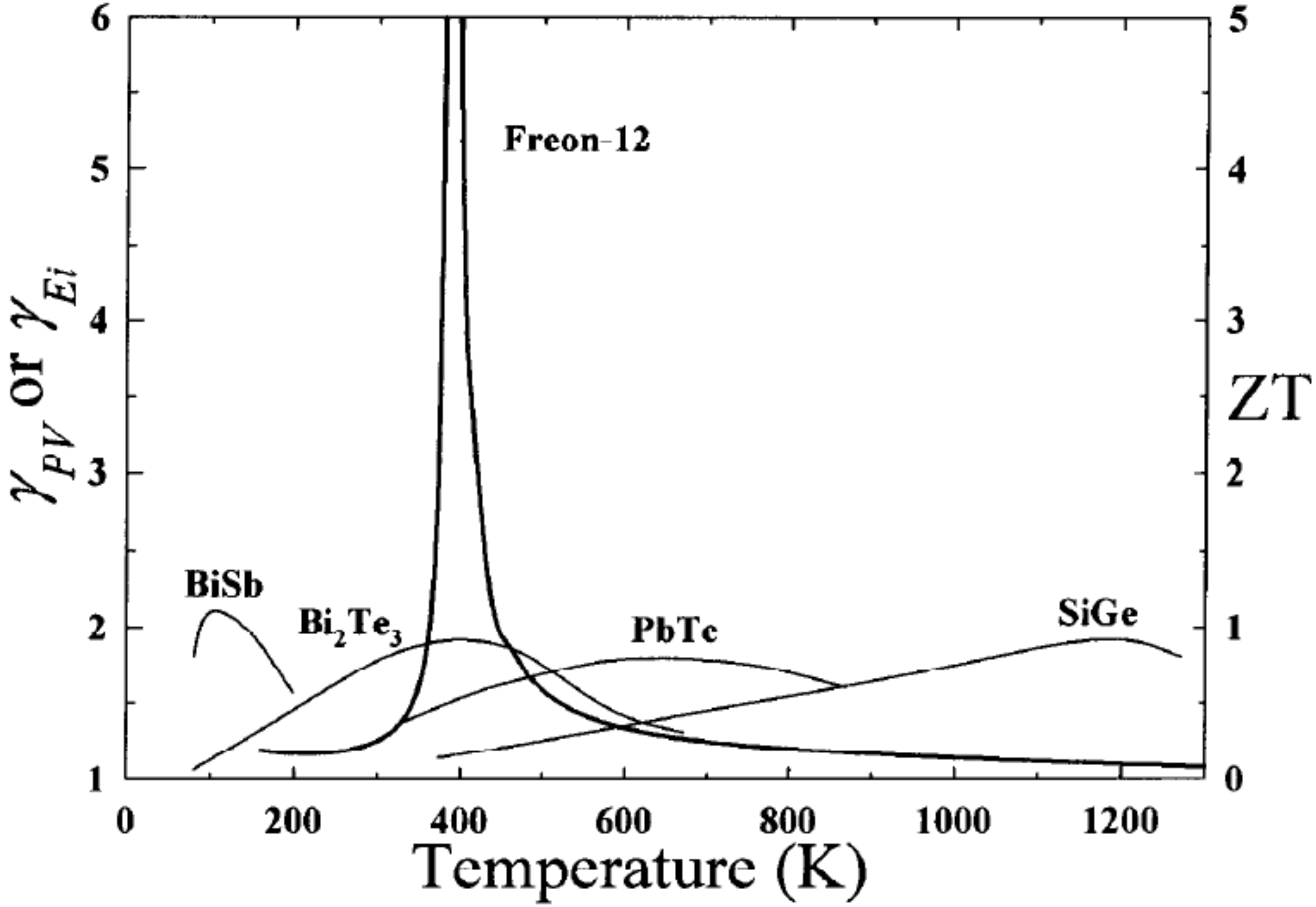
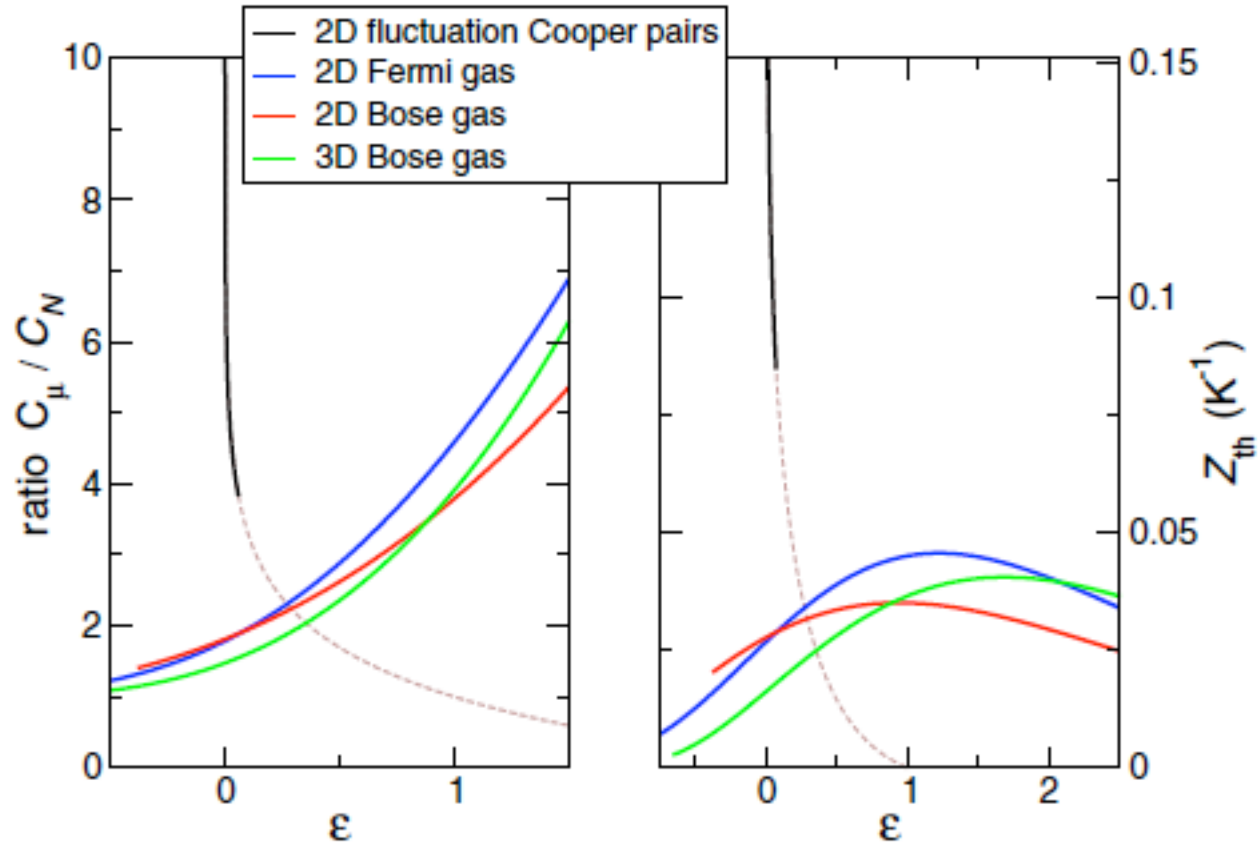


Fig. 4: Specific heat ratios, γ_{PV} for a *PV* system (Freon 12) and thermal conductivity ratios, γ_{Ei}=1+ZT, for selected n-type semiconductor alloys as a function of temperature.

(Vining, MRS Symp. **478**, 3 (1997))



$\epsilon = \ln T/T_c \approx (T - T_c)/T_c$

(Ouerdane et al., PRB **91**, 100501 (2015))

Power-efficiency trade-off:
Is it possible to overcome the non-interacting bound?

Noninteracting systems: for $P/P_{max} \ll 1$,

$$\eta(P) \le \eta_{\max}(P) = \eta_C \left(1 - B_q \sqrt{\frac{T_R}{T_L} \frac{P}{P_{\max}}}\right),$$

$$B_q \approx 0.478 \qquad (T_L > T_R)$$

Bound not favorable for power-efficiency trade-off; due to the fact that delta-energy filtering is the only mechanism to achieve Carnot for noninteracting systems

For interacting systems it is possible to achieve Carnot without delta-energy filtering

Interacting systems, Green-Kubo formula

The Green-Kubo formula expresses linear response transport coefficients in terms of dynamic correlation functions of the corresponding current operators, calculated at thermodynamic equilibrium

$$\lambda_{ab} = \lim_{\omega\to 0} \mathrm{Re}[\lambda_{ab}(\omega)]$$

$$\lambda_{ab}(\omega) = \lim_{\epsilon\to 0} \int_0^{\infty} dt e^{-i(\omega - i\epsilon)t} \lim_{\Omega\to\infty} \frac{1}{\Omega} \int_0^{\beta} d\tau \langle \hat{J}_a \hat{J}_b(t + i\tau)\rangle,$$

$$J_a = \langle \hat{J}_a \rangle$$

$$\hat{J}_a = \int_{\Omega} d\vec{r}\, \hat{j}_a(\vec{r})$$

$$\langle \cdot \rangle = \{\mathrm{tr}[(\cdot)\exp(-\beta H)]\} / \mathrm{tr}[\exp(-\beta H)]$$

$$\mathrm{Re}\lambda_{ab}(\omega) = 2\pi D_{ab}\delta(\omega) + \lambda_{ab}^{\mathrm{reg}}(\omega)$$

Non-zero generalized Drude weights signature of ballistic transport

Conservation laws and thermoelectric efficiency

Suzuki's formula (which generalizes Mazur's inequality) for finite-size Drude weights

$$d_{ab}(\Lambda) \equiv \frac{1}{2\Omega(\Lambda)} \lim_{\bar{t}\to\infty} \frac{1}{\bar{t}} \int_0^{\bar{t}} dt \langle \hat{J}_a(0)\hat{J}_b(t)\rangle = \frac{1}{2\Omega(\Lambda)} \sum_{m=1}^{M} \frac{\langle \hat{J}_a Q_m\rangle\langle \hat{J}_b Q_m\rangle}{\langle Q_m^2\rangle}$$

Q_m relevant (i.e., non-orthogonal to charge and thermal currents), mutually orthogonal conserved quantities

$$D_{ab} = \lim_{\bar{t}\to\infty} \lim_{\Lambda\to\infty} \frac{1}{2\Omega(\Lambda)\bar{t}} \int_0^{\bar{t}} dt \langle \hat{J}_a(0)\hat{J}_b(t)\rangle$$

Assuming commutativity of the two limits,

$$D_{ab} = \lim_{\Lambda\to\infty} d_{ab}(\Lambda)$$

Momentum-conserving systems

Consider systems with a single relevant constant of motion, notably momentum conservation

Ballistic contribution to $\det \boldsymbol{\lambda}$ vanishes since

$$D_{ee} D_{hh} - D_{eh}^2 = 0$$

$$\sigma \sim \lambda_{ee} \sim \Lambda$$

$$S \sim \lambda_{eh}/\lambda_{ee} \sim \Lambda^0 \qquad ZT = \frac{\sigma S^2}{\kappa} T \propto \Lambda^{1-\alpha} \to \infty \text{ when } \Lambda \to \infty$$

$$\kappa \sim \det \boldsymbol{\lambda}/L_{ee} \sim \Lambda^\alpha$$

$$(\alpha < 1)$$

(G.B., G. Casati, J. Wang, PRL 110, 070604 (2013))

For systems with more than a single relevant constant of motion, for instance for integrable systems, due to the Schwarz inequality

$$D_{ee}D_{hh} - D_{eh}^2 = ||\mathbf{x}_e||^2||\mathbf{x}_h||^2 - \langle \mathbf{x}_e, \mathbf{x}_h \rangle \geq 0$$

$$\mathbf{x}_i = (x_{i1}, ..., x_{iM}) = \frac{1}{2\Lambda}\left(\frac{\langle J_i Q_1 \rangle}{\sqrt{\langle Q_1^2 \rangle}}, ..., \frac{\langle J_i Q_M \rangle}{\sqrt{\langle Q_M^2 \rangle}}\right)$$

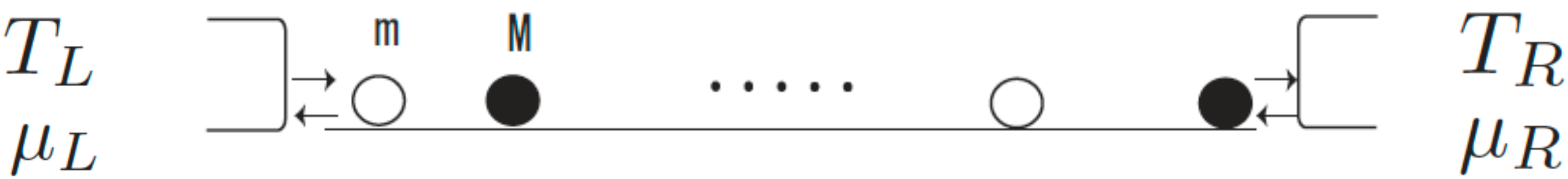
$$\langle \mathbf{x}_e, \mathbf{x}_h \rangle = \sum_{k=1}^{M} x_{ek} x_{hk}$$

Equality arises only in the exceptional case when the two vectors are parallel; in general

$$\det \lambda \propto \Lambda^2, \ \kappa \propto \Lambda, \ ZT \propto \Lambda^0$$

Example: 1D interacting classical gas

Consider a one dimensional gas of elastically colliding particles with unequal masses: m, M



For $M = m$ $\qquad J_u = T_L\gamma_L - T_R\gamma_R \qquad (J_u = J_q + \mu J_\rho)$

(integrable model) $\qquad J_\rho = \gamma_L - \gamma_R. \qquad ZT = 1$ (at $\mu = 0$)

For $M \neq m$ $\qquad$ ZT depends on the system size

Quantum mechanics needed: Relation between density and electrochemical potential

Reservoirs modeled as ideal (1D) gases

$$f_\alpha(v) = \sqrt{\frac{m}{2\pi k_B T_\alpha}} \exp\left(-\frac{mv^2}{2k_B T_\alpha}\right)$$

Maxwell-Bolzmann distribution of velocities

$$\gamma_\alpha = \rho_\alpha \int_0^\infty dv\, v\, f_\alpha(v) = \rho_\alpha \sqrt{\frac{k_B T_\alpha}{2\pi m}}$$

injection rates

$$\Xi_\alpha = \sum_{N=0}^{\infty} \frac{1}{N!} \left\{ \frac{\Lambda}{h} e^{\beta_\alpha \mu_\alpha} \int dv\, m \exp\left[-\beta_\alpha \left(\frac{1}{2} m v^2\right)\right]\right\}^N$$

grand partition function

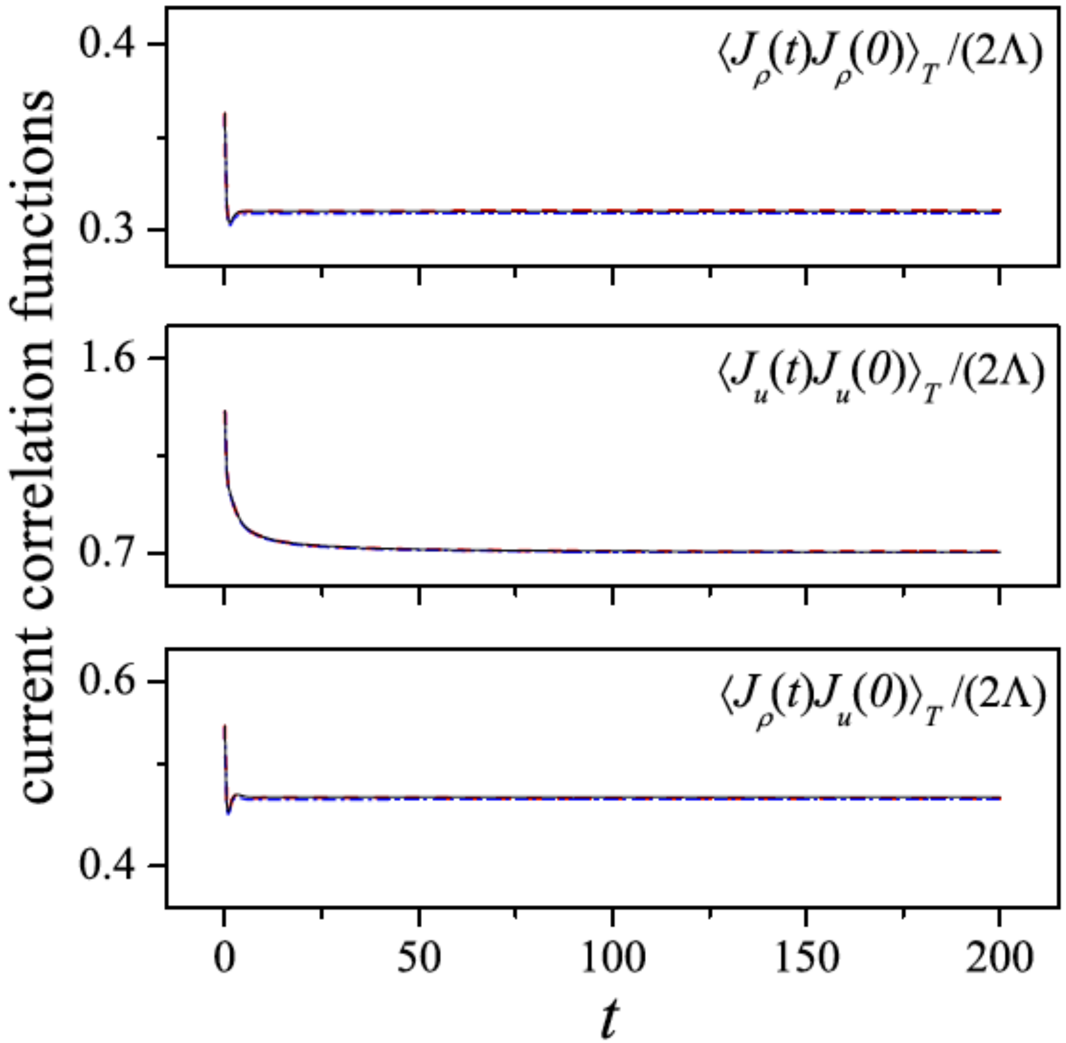
$$\langle N \rangle_\alpha = \frac{1}{\beta_\alpha} \frac{\partial}{\partial \mu_\alpha} \ln \Xi_\alpha, \quad \rho_\alpha = \frac{\langle N \rangle_\alpha}{\Lambda} = \frac{e^{\beta_\alpha \mu_\alpha} \sqrt{2\pi m k_B T_\alpha}}{h}$$

density

$$\mu_\alpha = k_B T_\alpha \ln(\lambda_\alpha \rho_\alpha), \quad \lambda_\alpha = \frac{h}{\sqrt{2\pi m k_B T_\alpha}}$$

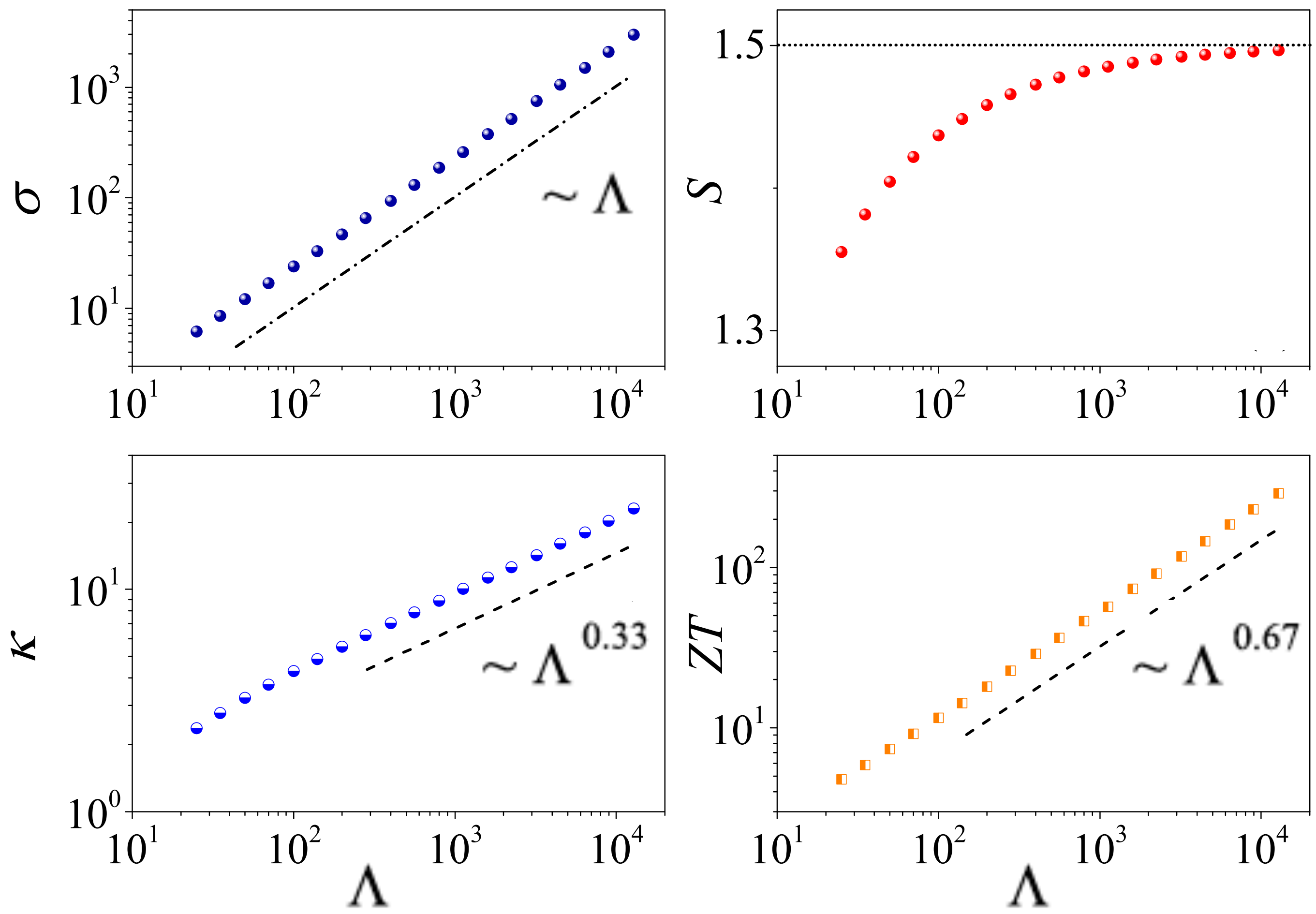
de Broglie thermal wave length

Non-decaying correlation functions



$\Lambda = 256$ (red dashed curve), 512 (blue dash-dotted curve), and 1024 (black solid curve)

Carnot efficiency at the thermodynamic limit



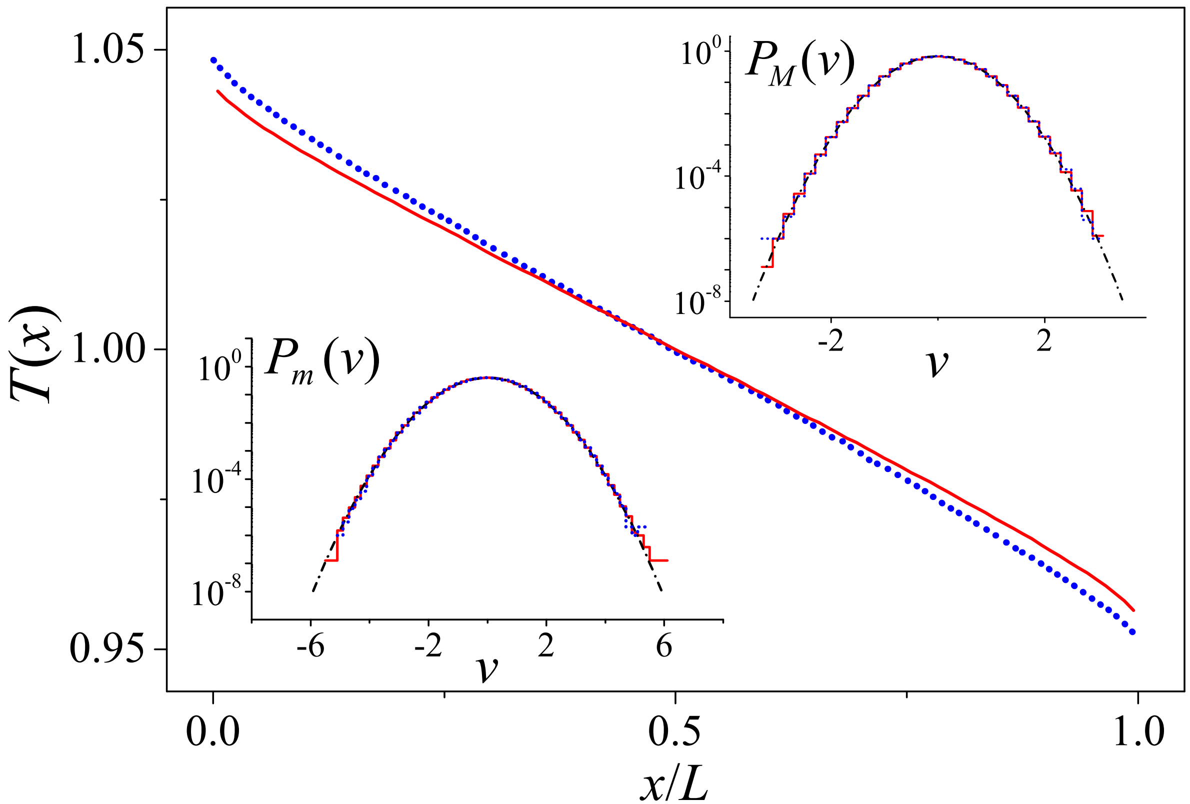
Anomalous thermal transport

$$ZT = \frac{\sigma S^2}{k} T$$

ZT diverges increasing the systems size

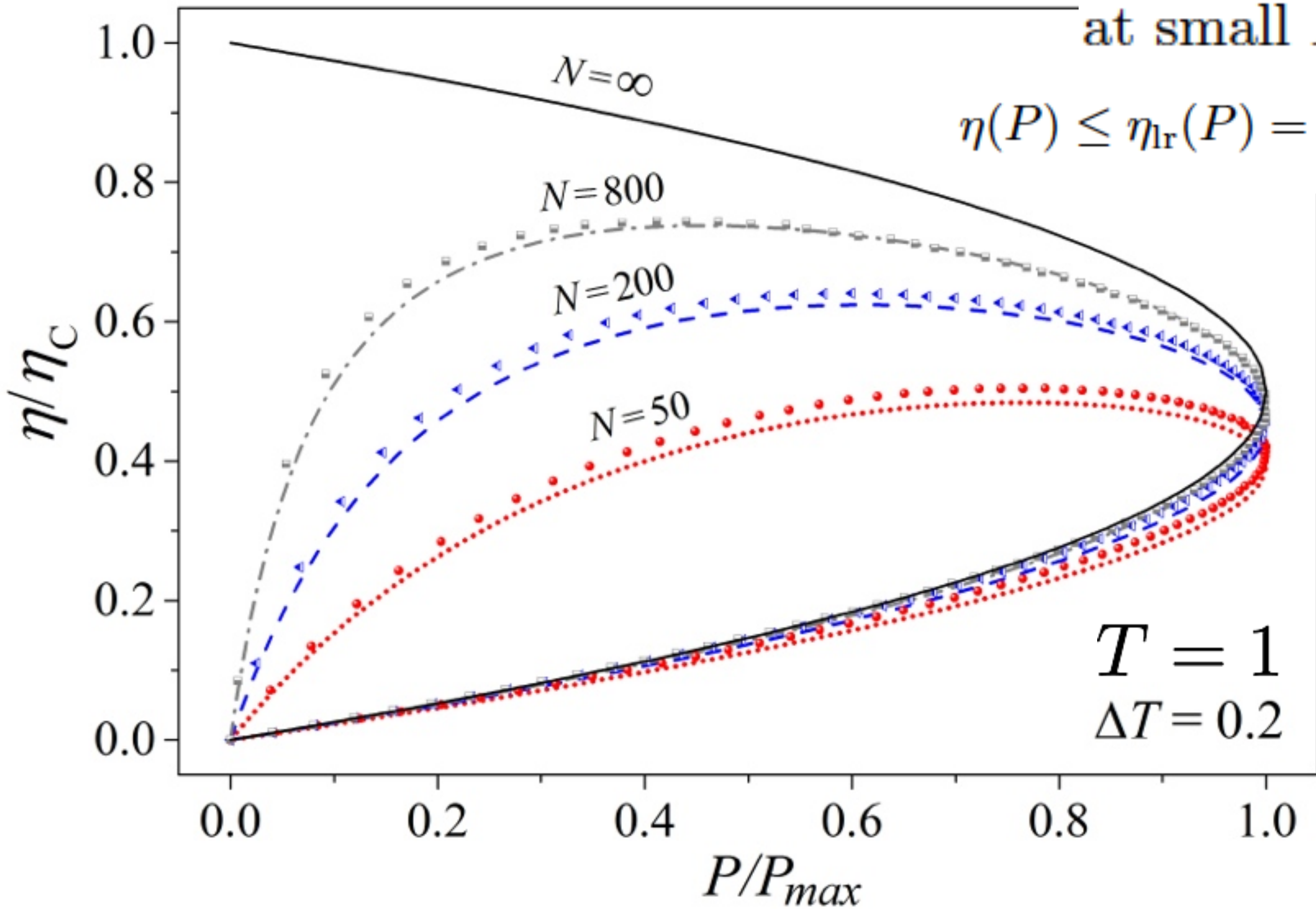
[R. Luo, G. B., G. Casati, J. Wang, PRL **121**, 080602 (2018)]

Delta-energy filtering mechanism?



A mechanism for achieving Carnot different from delta-energy filtering is needed

Validity of linear response



at small $P/P_{\max}$

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

The agreement with linear response improves with N

(∇T decreases as the system size increases)

Non-interacting classical bound (but quantum mechanics needed)

$$J_\rho = \gamma_L \int_0^\infty d\epsilon u_L(\epsilon)\mathcal{T}(\epsilon) - \gamma_R \int_0^\infty d\epsilon u_R(\epsilon)\mathcal{T}(\epsilon), \quad u_\alpha(\epsilon) \;=\; \beta_\alpha e^{-\beta_\alpha \epsilon}$$

$$J_e = \frac{e}{h}\int_0^\infty dE\,[f_L(E) - f_R(E)]\tau(E)$$ charge current

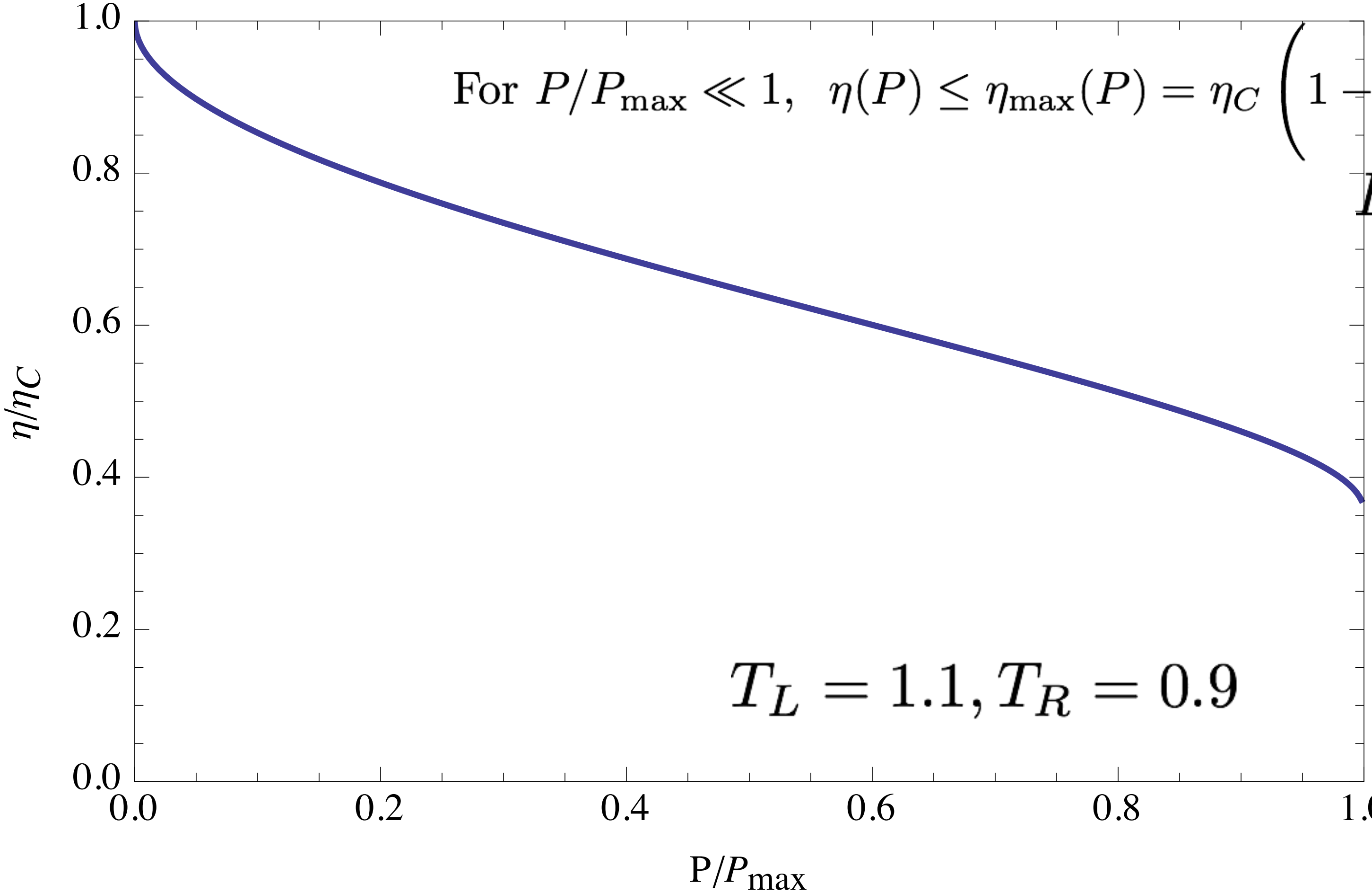
$$J_{h,\alpha} = \frac{1}{h}\int_0^\infty dE\,(E-\mu_\alpha)[f_L(E) - f_R(E)]\tau(E)$$ heat current

$$f_\alpha(E) = e^{-\beta_\alpha(E-\mu_\alpha)}$$ Maxwell-Boltzmann distribution

$$0 \leq \tau(E) \leq 1$$ (in 1D)

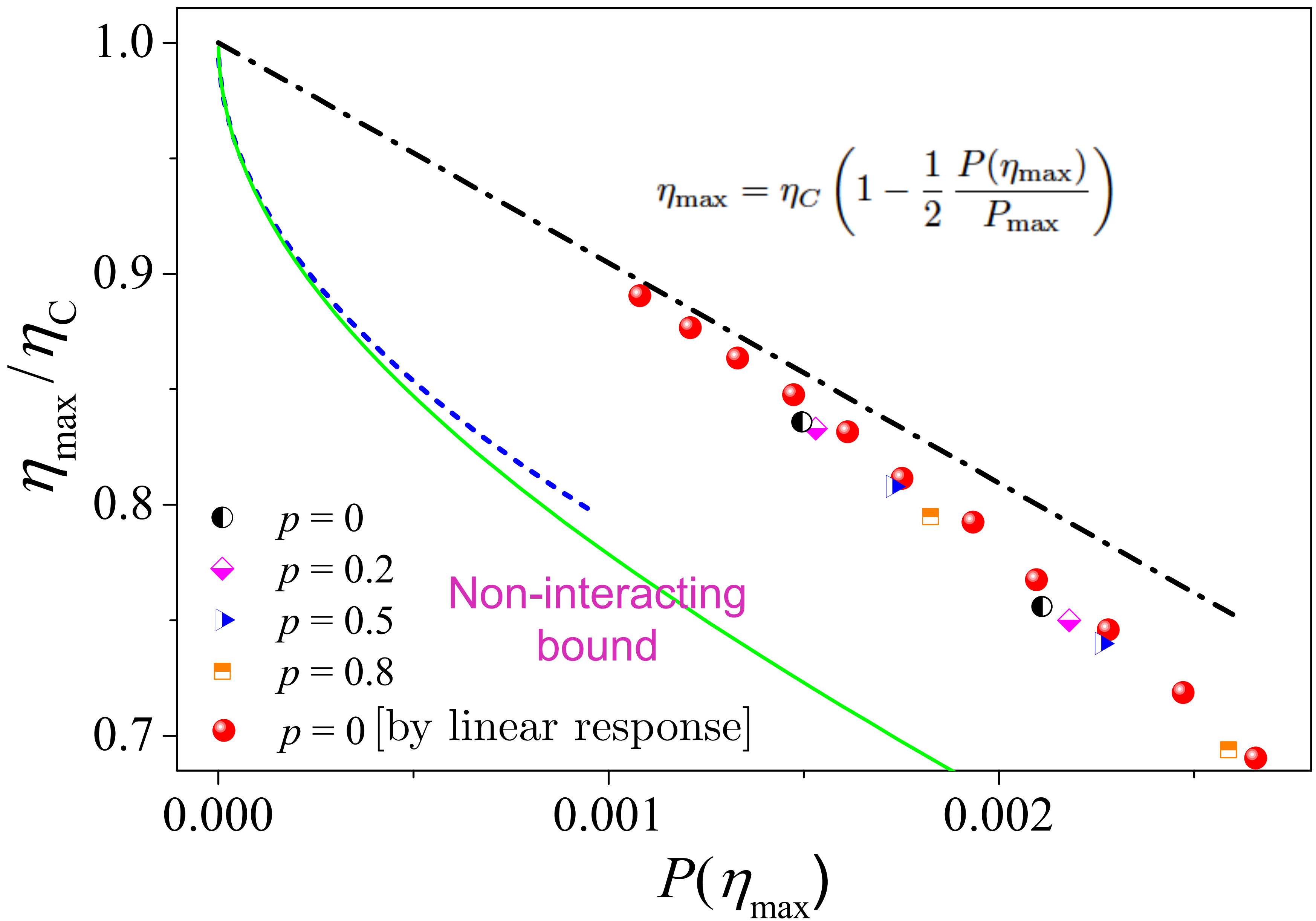
$$\text{For } P/P_{\max} \ll 1, \;\; \eta(P) \le \eta_{\max}(P) = \eta_C \left(1 - B_c \sqrt{\frac{T_R}{T_L}\frac{P}{P_{\max}}}\right),$$

$$B_c \approx 0.493$$



$$P \le P_{\max} = A_c \frac{\pi^2}{h} k_B^2 (\Delta T)^2, \quad A_c \approx 0.0373$$

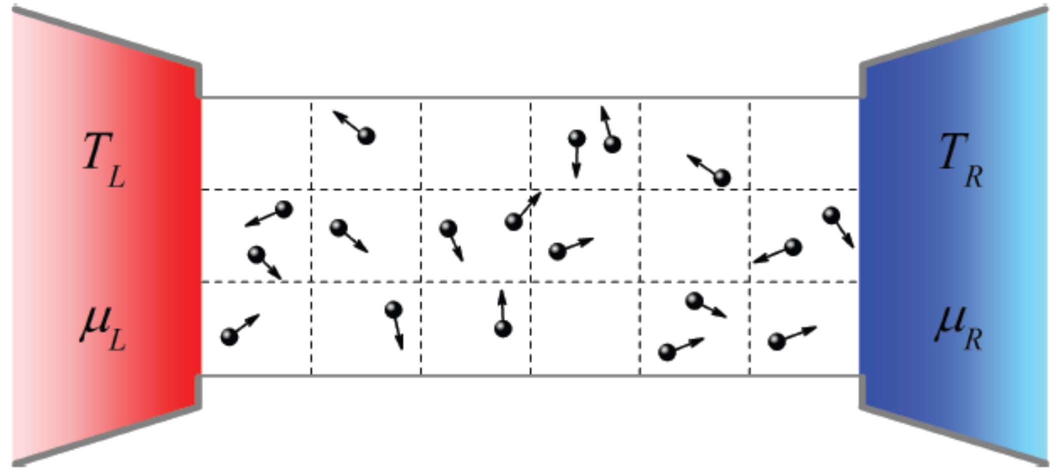
Overcoming the non-interacting bound



Multiparticle collision dynamics (Kapral model) in 2D

<u>Streaming step:</u> free propagation during a time τ

$$\vec{r}_i \longrightarrow \vec{r}_i + \vec{v}_i \tau$$

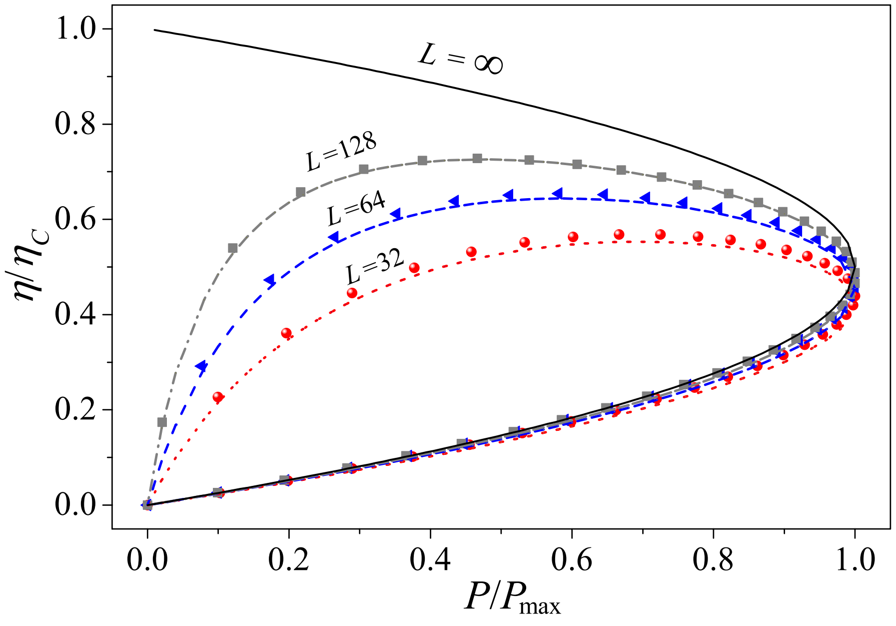


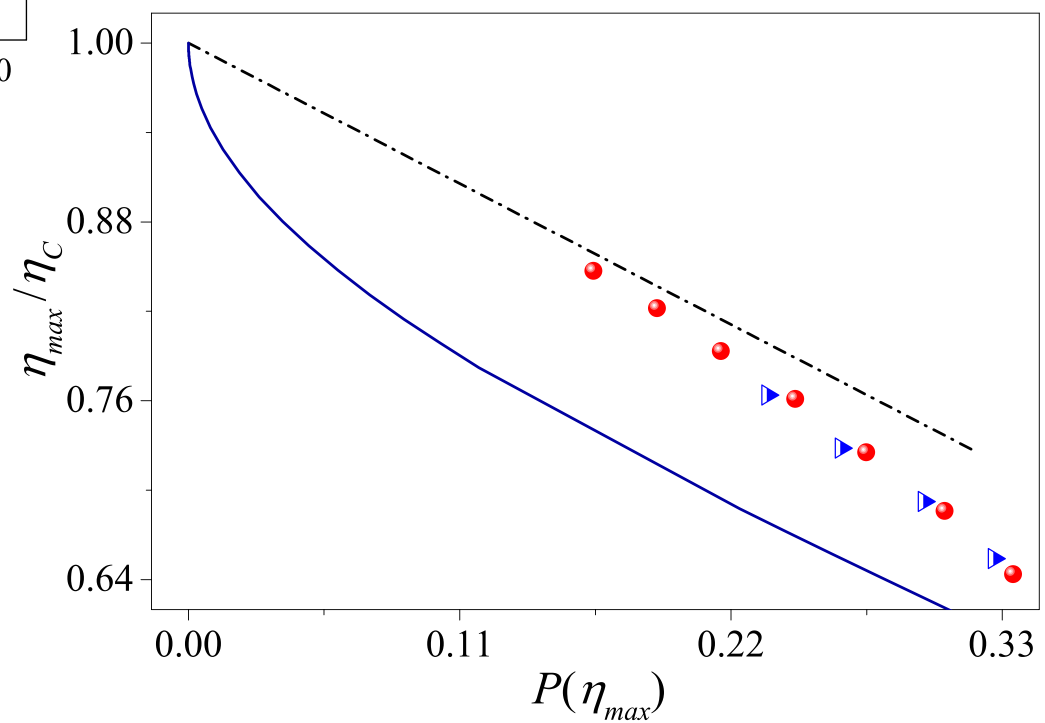
<u>Collision step:</u> random rotations of the velocities of the particles in cells of linear size *a* with respect to the center of mass velocity:

$$\vec{v}_i \longrightarrow \vec{V}_{\mathrm{CM}} + \hat{\mathcal{R}}^{\pm\alpha}\left(\vec{v}_i - \vec{V}_{\mathrm{CM}}\right)$$

Momentum is conserved

Overcoming the (2D) non-interacting bound

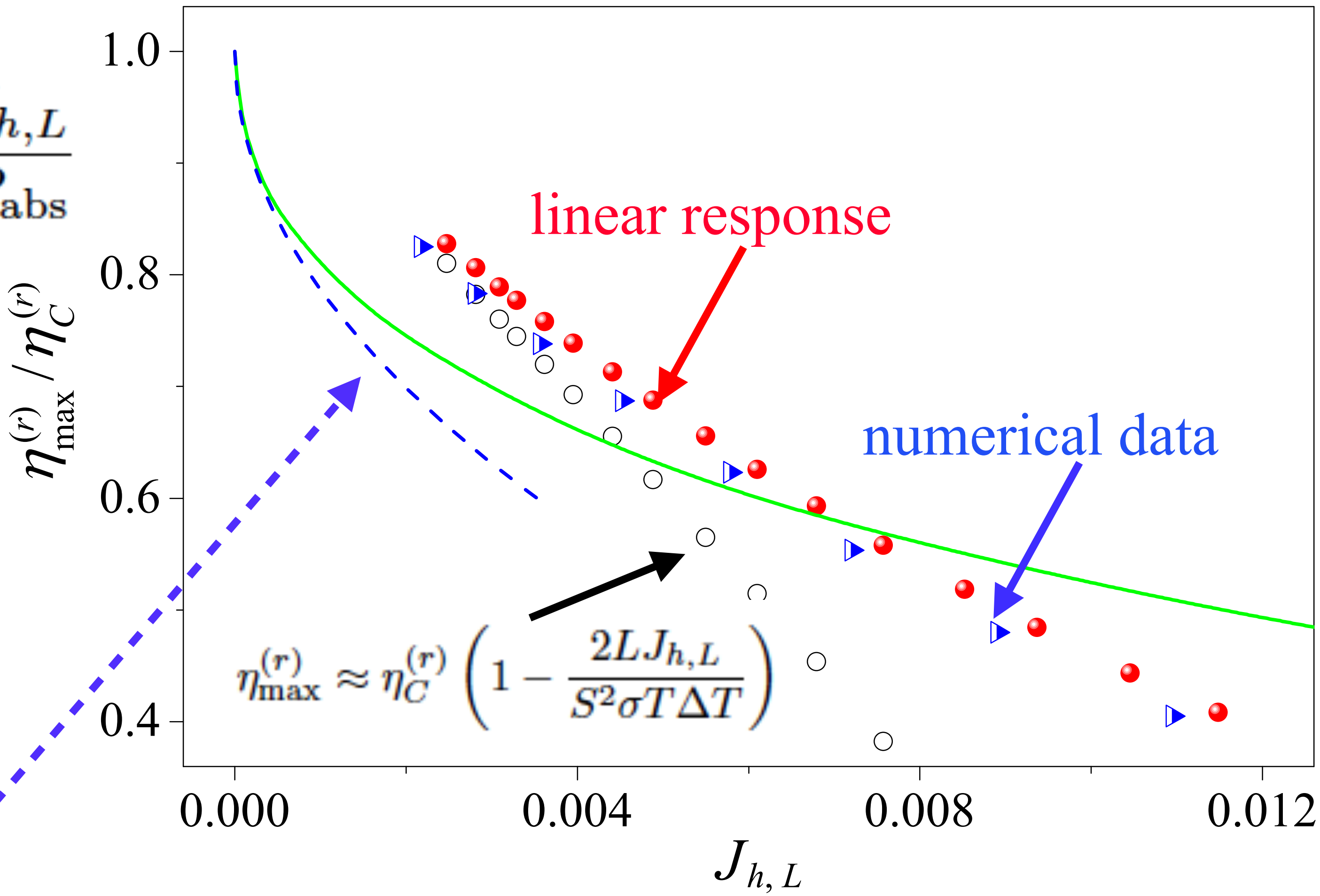




Results can be extended to cooling

COP

$$\eta^{(r)} = \frac{J_{h,L}}{P_{\mathrm{abs}}}$$



$$\eta^{(r)} \le \eta^{(r,\mathrm{st})}_{\mathrm{max}}(J_{h,L}) \approx \eta^{(r)}_C \left(1 - C\sqrt{\frac{T_R}{T_R - T_L}\frac{J_{h,L}}{(J_{h,L})^{(\mathrm{st})}_{\mathrm{max}}}}\right), \qquad (J_{h,L})^{(\mathrm{st})}_{\mathrm{max}} = \frac{k_B^2 T_L^2}{h}$$

$$C \approx 0.813$$

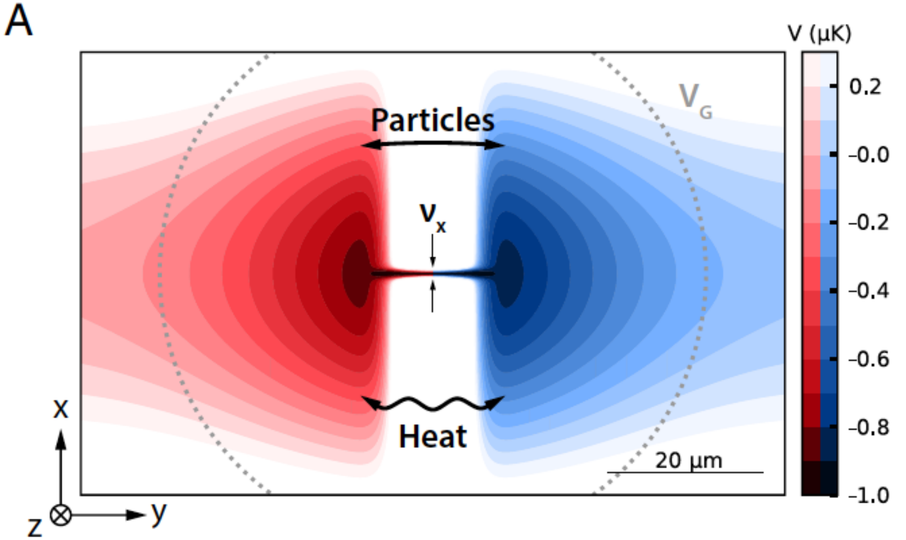
Applications for cold atoms?

Breakdown of the Wiedemann–Franz law in a unitary Fermi gas

Dominik Husmann[a], Martin Lebrat[a], Samuel Häusler[a], Jean-Philippe Brantut[b], Laura Corman[a,1], and Tilman Esslinger[a]

We report on coupled heat and particle transport measurements through a quantum point contact (QPC) connecting two reservoirs of resonantly interacting, finite temperature Fermi gases. After heating one of them, we observe a particle current flowing from cold to hot. We monitor the temperature evolution of the reservoirs and find that the system evolves after an initial response into a nonequilibrium steady state with finite temperature and chemical potential differences across the QPC. In this state any relaxation in the form of heat and particle currents vanishes. From our measurements we extract the transport coefficients of the QPC and deduce a Lorenz number violating the Wiedemann–Franz law by one order of magnitude, a characteristic persisting even for a wide contact. In contrast, the Seebeck coefficient takes a value close to that expected for a noninteracting Fermi gas and shows a smooth decrease as the atom density close to the QPC is increased beyond the superfluid transition. Our work represents a fermionic analog of the fountain effect observed with superfluid helium and poses challenges for microscopic modeling of the finite temperature dynamics of the unitary Fermi gas.

A



PNAS | August 21, 2018 | vol. 115 | no. 34 | 8563–8568

Power-efficiency trade-off at the verge of phase transitions

For heat engines described as Markov processes:

$$P \leq A(\eta_C - \eta)$$

[N. Shiraishi, K. Saito, H. Tasaki, PRL **117**, 190601 (2016)]

For a working substance at a critical point:

$$(\eta - \eta_C) \sim N^{-a} \to 0 \,(\text{with}\, a > 0), \qquad P \sim N$$

[M. Campisi, R. Fazio, Nature Comm. **7**, 11895 (2016); see also Allahverdyan et al., PRL **111**, 050601 (2013)]

Results compatible only with diverging amplitude A when approaching the Carnot efficiency

Power-efficiency-fluctuations trade-off

For classical Markovian dynamics on a finite set of states and overdamped Langevin dynamics, trade-off between power, efficiency, and constancy for steady-state engines:

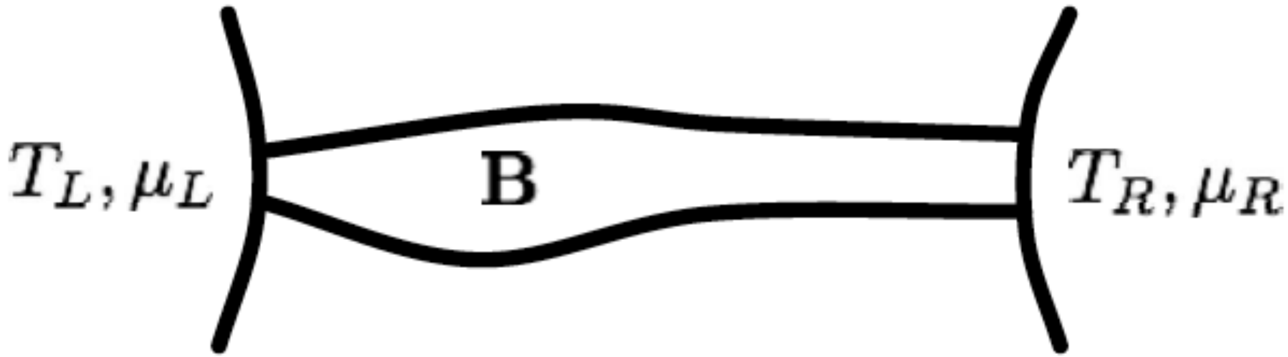
$$P \frac{\eta}{\eta_C - \eta} \frac{T_c}{\Delta_P} \leq \frac{1}{2} \qquad \Delta_P \equiv \lim_{t \to \infty} \langle (P(t) - P)^2 \rangle t$$

[P. Pietzonka, U. Seifert, PRL **120**, 190602 (2018)]

Bound violated in quantum mechanics, e.g. for resonant tunnelling transport (noninteracting system), but not close to Carnot efficiency. The problem for interacting systems is open.

[J. Liu. D. Segal, PRE **99**, 062141 (2019)]

Carnot efficiency at finite power with broken time-reversal symmetry?



$$\begin{cases} J_e = L_{ee}(\mathbf{B})\mathcal{F}_e + L_{eh}(\mathbf{B})\mathcal{F}_h \\ J_h = L_{he}(\mathbf{B})\mathcal{F}_e + L_{hh}(\mathbf{B})\mathcal{F}_h \end{cases}$$

$$\mathcal{F}_e = \Delta V/T \quad (\Delta V = \Delta\mu/e)$$

$$\mathcal{F}_h = \Delta T/T^2$$

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

$$\Delta T = T_L - T_R$$

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

(we assume $T_L > T_R, \;\; \mu_L < \mu_R$)

Constraints from thermodynamics

POSITIVITY OF THE ENTROPY PRODUCTION:

$$\dot{\mathscr{S}} = \mathfrak{F}_e J_e + \mathfrak{F}_h J_h \geq 0 \quad \Rightarrow \quad \begin{aligned} &L_{ee} \geq 0 \\ &L_{hh} \geq 0 \\ &L_{ee} L_{hh} - \frac{1}{4}(L_{eh} + L_{he})^2 \geq 0 \end{aligned}$$

ONSAGER-CASIMIR RELATIONS:

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

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

Both maximum efficiency and efficiency at maximum power depend on two parameters

$$x = \frac{L_{eh}}{L_{he}} = \frac{S(\boldsymbol{B})}{S(-\boldsymbol{B})}$$

$$y = \frac{L_{eh}L_{he}}{\det \boldsymbol{L}} = \frac{G(\boldsymbol{B})S(\boldsymbol{B})S(-\boldsymbol{B})}{K(\boldsymbol{B})}T$$

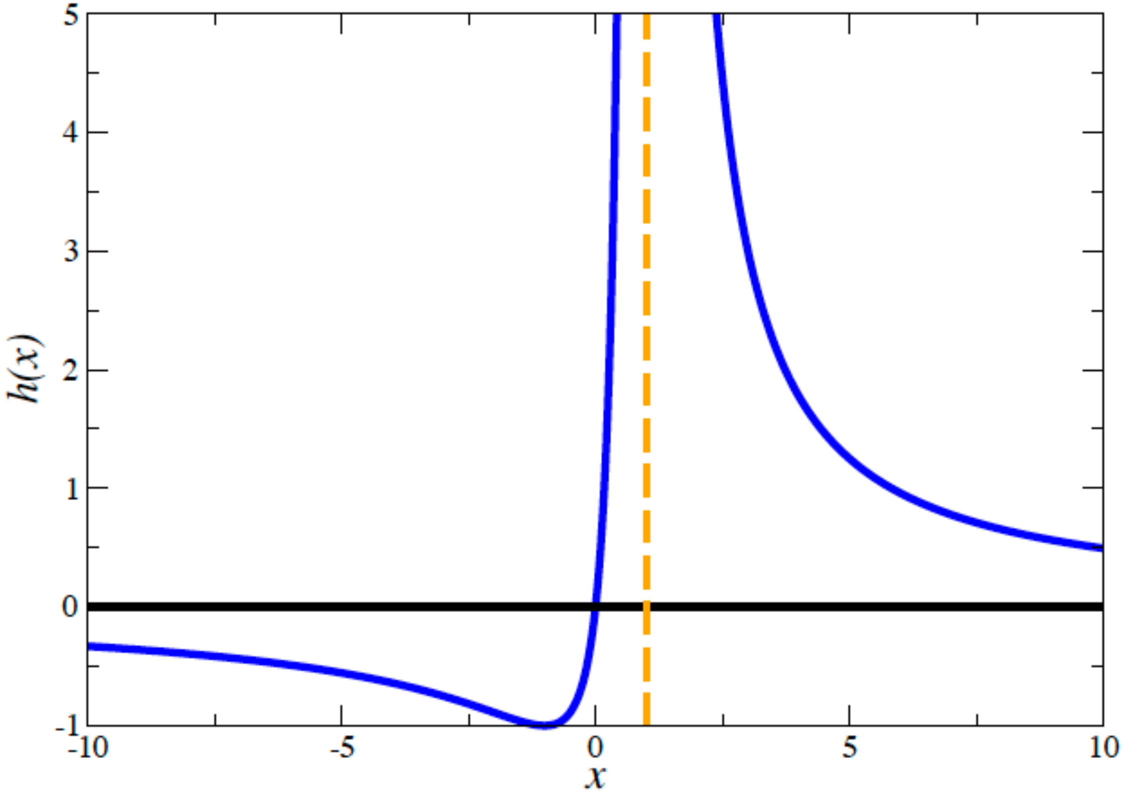
$$\eta(P_{\max}) = \frac{\eta_C}{2}\frac{xy}{2+y} \qquad \eta_{\max} = \eta_C\, x\, \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1}$$

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

asymmetry parameter $x = 1$

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

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

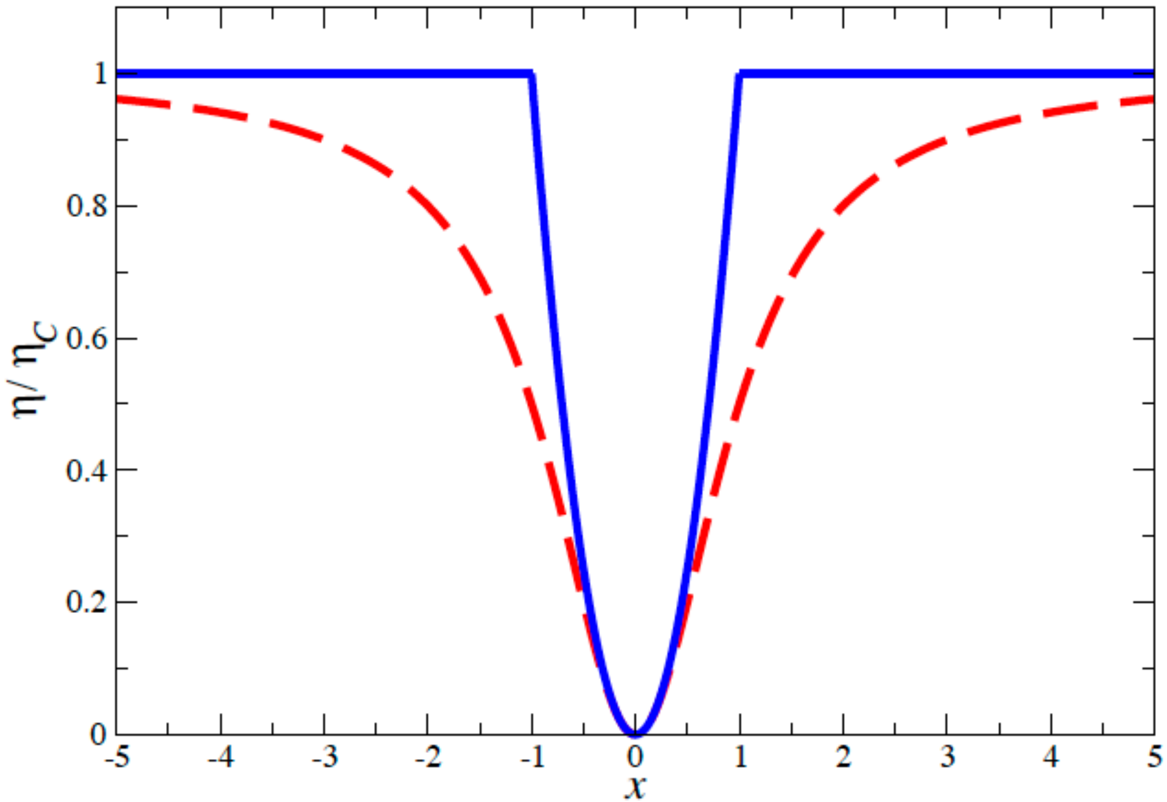


$$h(x) = 4x/(x-1)^2$$

maximum efficiencies

achieved for $y = h(x)$

$$\bar{\eta}(P_{\max}) = \eta_C \frac{x^2}{x^2+1}\,, \qquad \bar{\eta}_{\max} = \begin{cases} \eta_C\, x^2 \ \text{ if } |x| \leq 1\,, \\ \eta_C \quad \text{ if } |x| \geq 1\,. \end{cases}$$



The CA limit can be overcome within linear response

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

Carnot efficiency could be obtained far from the tight coupling condition

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

Output power at maximum efficiency

$$P(\bar{\eta}_{\max}) = \frac{\bar{\eta}_{\max}}{4} \frac{|L_{eh}^2 - L_{he}^2|}{L_{ee}} \mathcal{F}_h$$

When time-reversibility is broken, <u>within linear response</u> it is not forbidden from the second law 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 could in principle find small enough forces such that the linear theory holds.

Reversible part of the currents

$$J_i^{\mathrm{rev}} = \sum_{j=e,h} \frac{L_{ij} - L_{ji}}{2} \mathfrak{F}_j$$

$$J_i^{\mathrm{irr}} = \sum_{j=e,h} \frac{L_{ij} + L_{ji}}{2} \mathfrak{F}_j$$

The reversible part of the currents does not contribute to entropy production

$$\dot{\mathscr{S}} = \mathfrak{F}_e J_e + \mathfrak{F}_h J_h = J_e^{\mathrm{irr}} \mathfrak{F}_e + J_h^{\mathrm{irr}} \mathfrak{F}_h$$

Possibility of dissipationless transport?

[K.. Brandner, K. Saito, U. Seifert, PRL **110**, 070603 (2013)]

How to obtain asymmetry in the Seebeck coefficient?

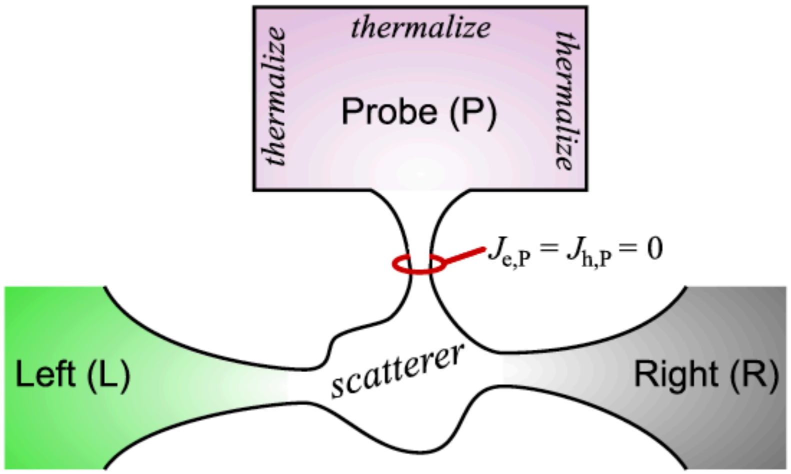
For non-interacting systems, due to the symmetry properties of the scattering matrix ⇒ $S(\mathbf{B}) = S(-\mathbf{B})$

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

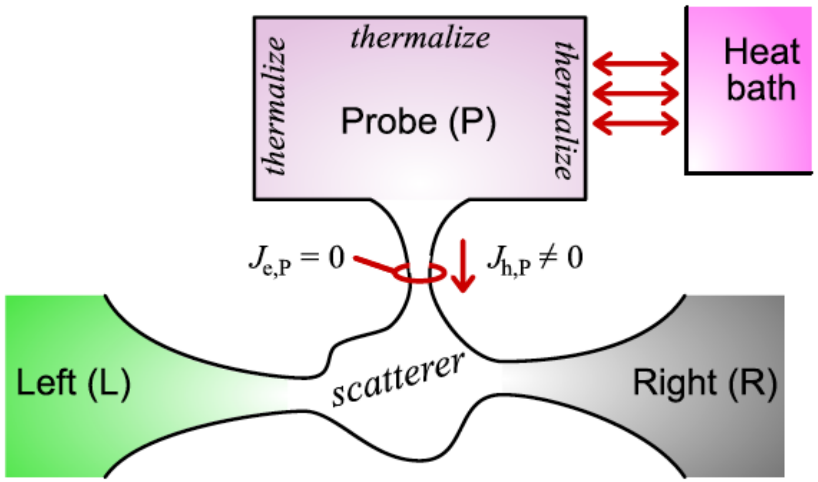
Let us consider the case of partially coherent transport, with inelastic processes simulated by "conceptual probes" (Buttiker, 1988).

Physical model of probe reservoirs

Large but finite "reservoirs"

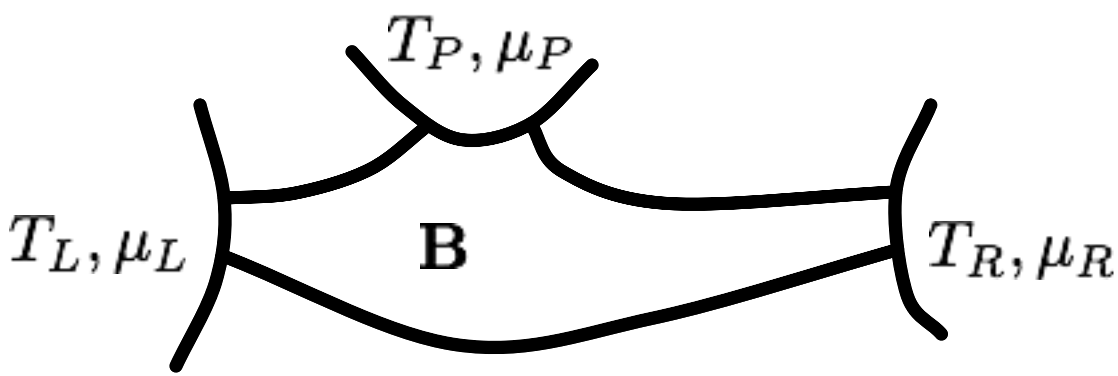


Voltage and temperature probe (mimicking e-e inelastic scattering)



Voltage probe (mimicking e-ph inelastic scattering)

Non-interacting three-terminal model



P probe reservoir

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

Charge and energy conservation:

$$\sum_k J_{e,k} = 0,\ \sum_k J_{u,k} = 0 \qquad (J_{h,k} = J_{u,k} - (\mu/e) J_{e,k})$$

Entropy production (linear response):

$$\dot{\mathscr{S}} = {}^t\boldsymbol{\mathcal{F}}\mathbf{J} = \sum_{i=1}^{4} J_i \mathcal{F}_i$$

$${}^t\mathbf{J} = (J_{eL}, J_{hL}, J_{eP}, J_{hP})$$

$${}^t\boldsymbol{\mathcal{F}} = \left(\frac{\Delta\mu}{eT}, \frac{\Delta T}{T^2}, \frac{\Delta\mu_P}{eT}, \frac{\Delta T_P}{T^2} \right)$$

Three-terminal Onsager matrix

Equation connecting fluxes and thermodynamic forces:

$$\mathbf{J} = \mathbf{L}\boldsymbol{\mathcal{F}}$$

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

In block-matrix form:

$$\begin{pmatrix} \mathbf{J}_\alpha \\ \mathbf{J}_\beta \end{pmatrix} = \begin{pmatrix} \mathbf{L}_{\alpha\alpha} & \mathbf{L}_{\alpha\beta} \\ \mathbf{L}_{\beta\alpha} & \mathbf{L}_{\beta\beta} \end{pmatrix} \begin{pmatrix} \boldsymbol{\mathcal{F}}_\alpha \\ \boldsymbol{\mathcal{F}}_\beta \end{pmatrix}$$

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

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

Two-terminal Onsager matrix for partially coherent transport

Reduction to 2x2 Onsager matrix when the third terminal is a probe terminal mimicking inelastic scattering

$$\mathbf{J}_\alpha = \mathbf{L}'\boldsymbol{\mathcal{F}}_\alpha, \quad \mathbf{L}' \equiv \mathbf{L}_{\alpha\alpha} - \mathbf{L}_{\alpha\beta}\mathbf{L}_{\beta\beta}{}^{-1}\mathbf{L}_{\beta\alpha}.$$

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} L'_{11} & L'_{12} \\ L'_{21} & L'_{22} \end{pmatrix} \begin{pmatrix} \mathcal{F}_1 \\ \mathcal{F}_2 \end{pmatrix}$$

$\mathbf{L}'$ 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

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

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

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

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

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

Onsager coefficients from linear response expansion of the currents

Transmission probabilities:

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

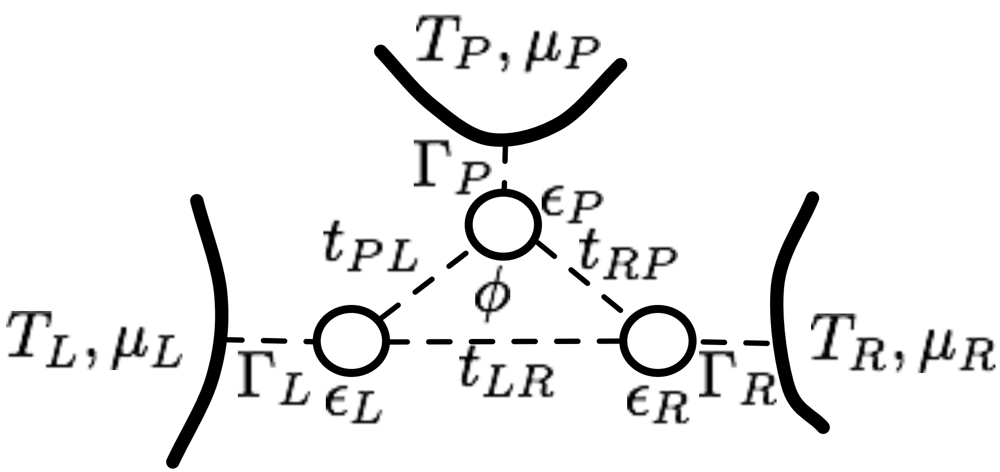
Broadening functions $\Gamma_k(E) \equiv i[\Sigma_k(E) - \Sigma_k^\dagger(E)]$

Self-energies Σ_k

Retarded system's Green function

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

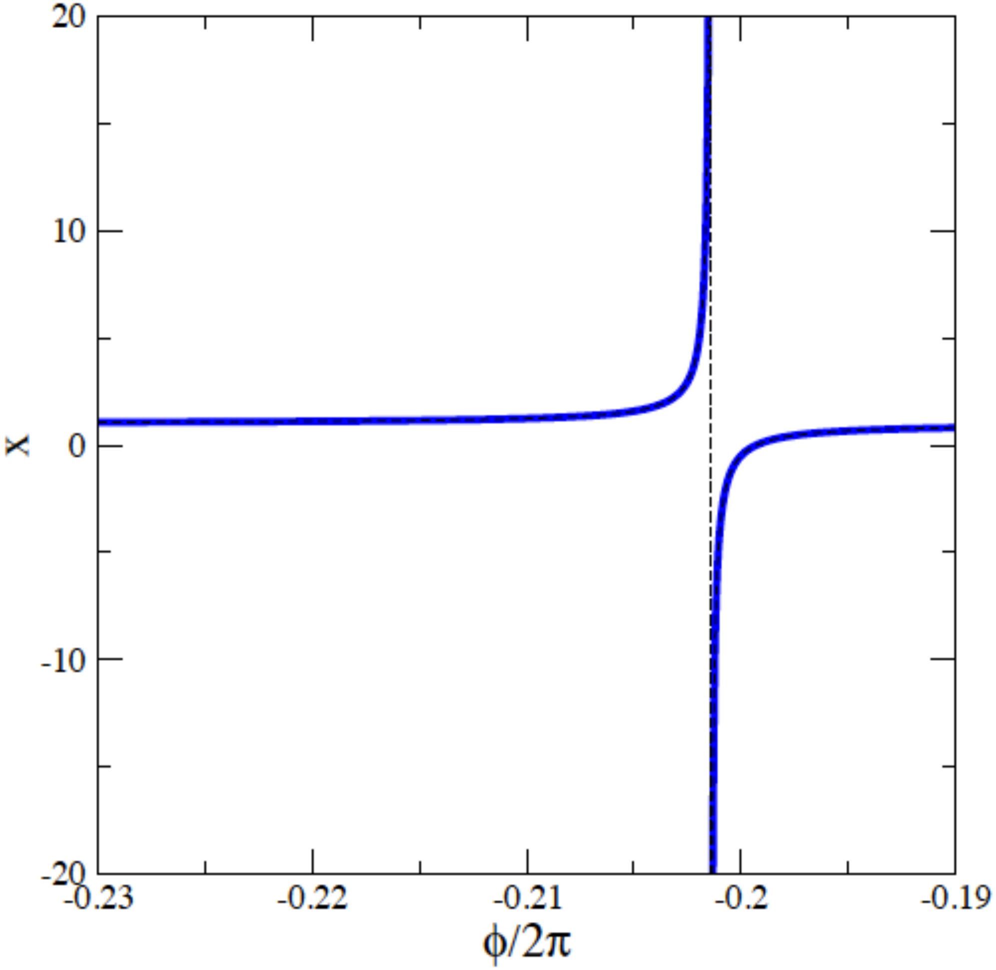
Illustrative three-dot example



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

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

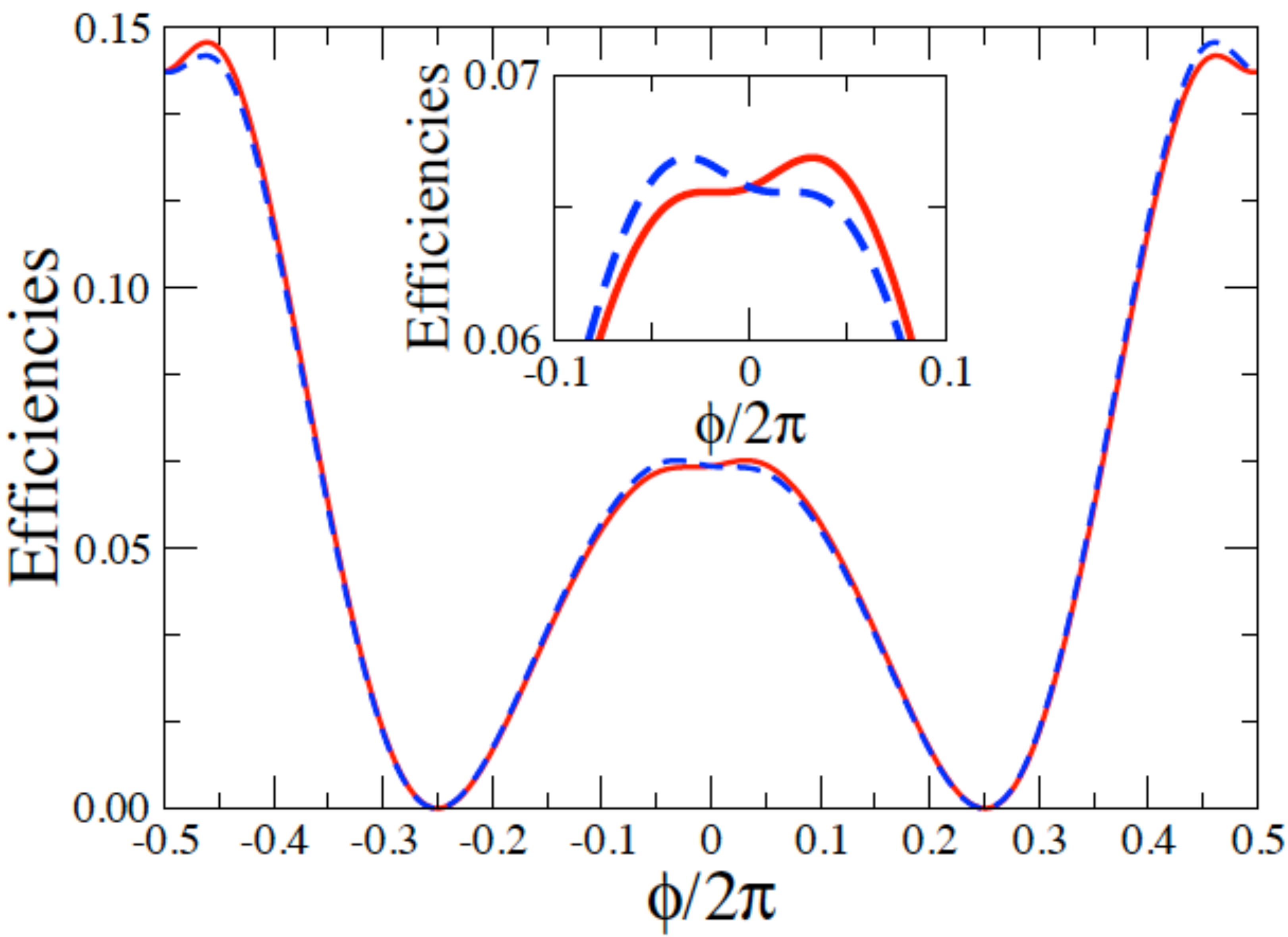
When a magnetic field is added, the efficiencies of power generation and refrigeration are no longer equal:

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

To linear order in the applied magnetic field:

$$\frac{1}{2}\left[\frac{\eta_{\max}(\boldsymbol{B})}{\eta_C} + \frac{\eta_{\max}^{(r)}(\boldsymbol{B})}{\eta_C^{(r)}}\right] = \frac{\eta_{\max}(\mathbf{0})}{\eta_C} = \frac{\eta_{\max}^{(r)}(\mathbf{0})}{\eta_C^{(r)}}$$

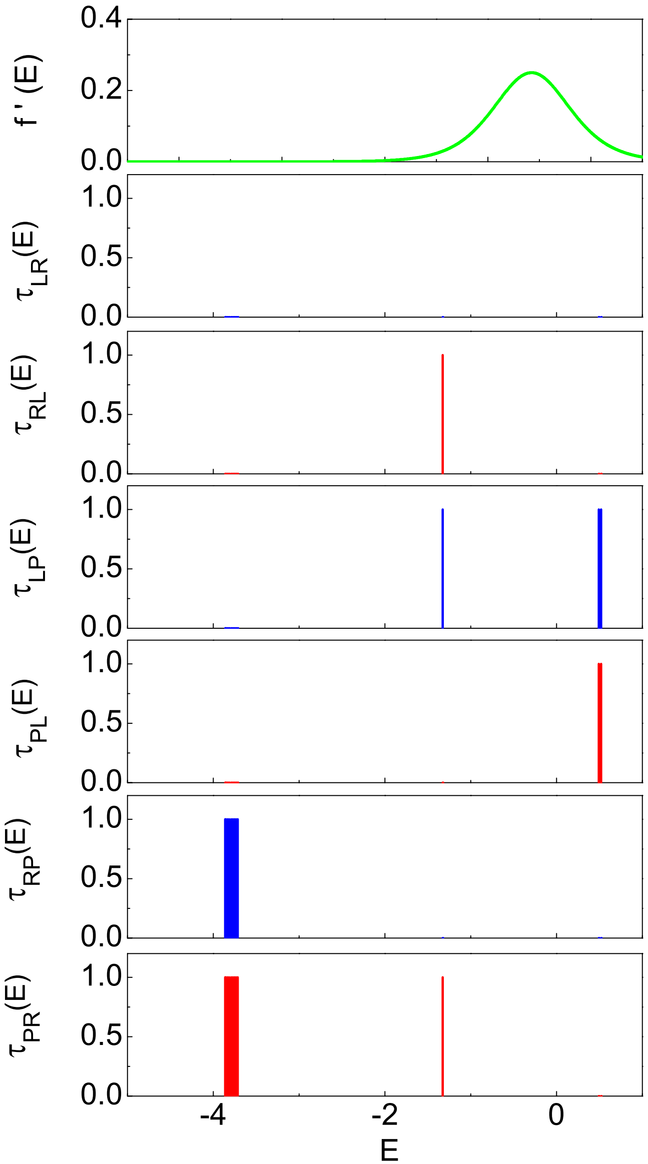
A small magnetic field improves either power generation or refrigeration, and vice versa if we reverse the direction of the field



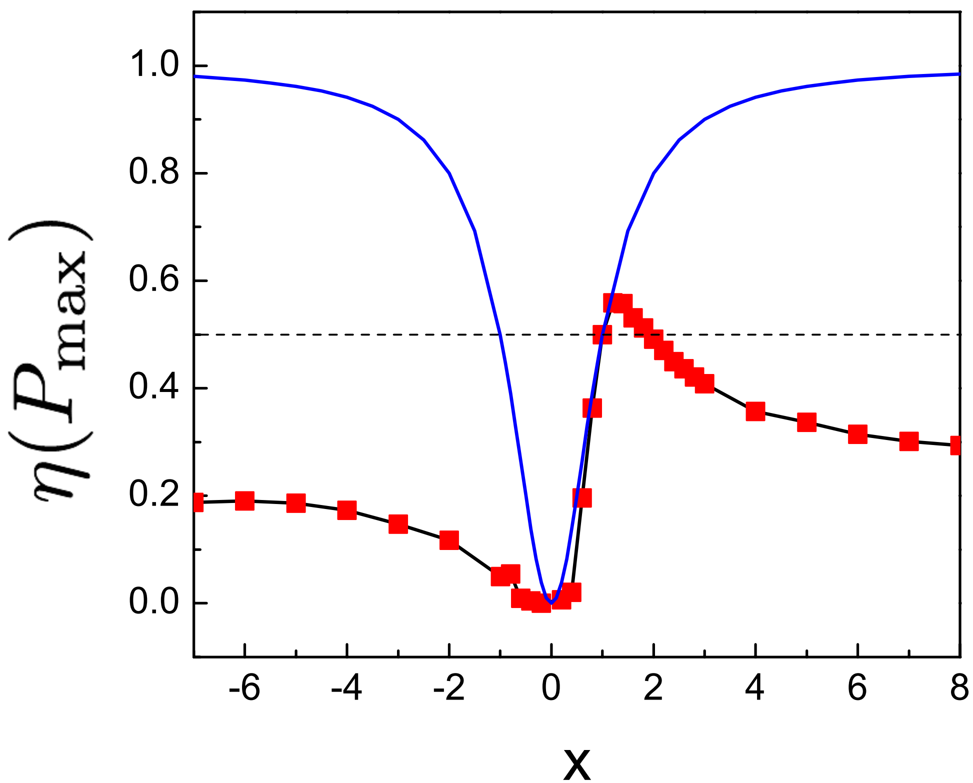
The large-field enhancement of efficiencies is model-dependent, but the small-field asymmetry is generic

Transmission windows model

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



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

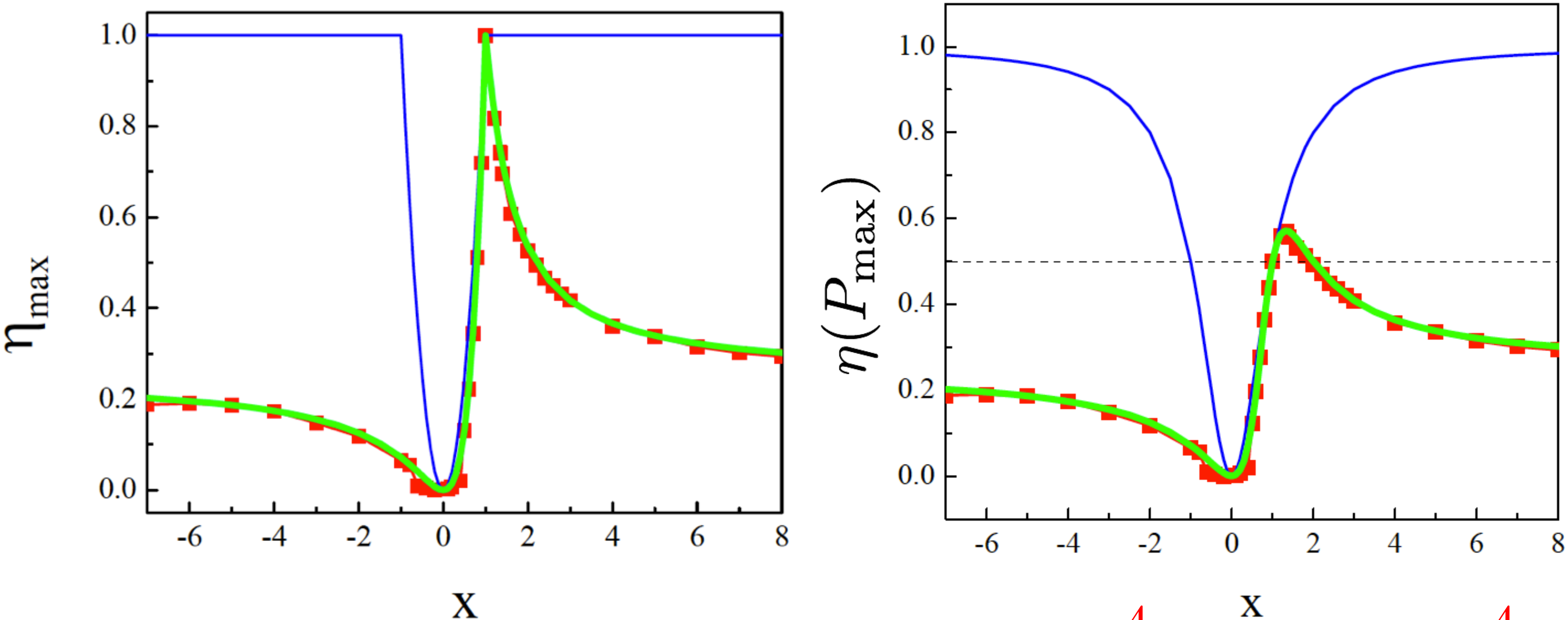


[V.. Balachandran, G. B., G. Casati, PRB **87**, 165419 (2013);
se also M. Horvat, T. Prosen, G. B., G. Casati, PRE **86**, 052102 (2012)]

Saturation of bounds from the unitarity of S-matrix

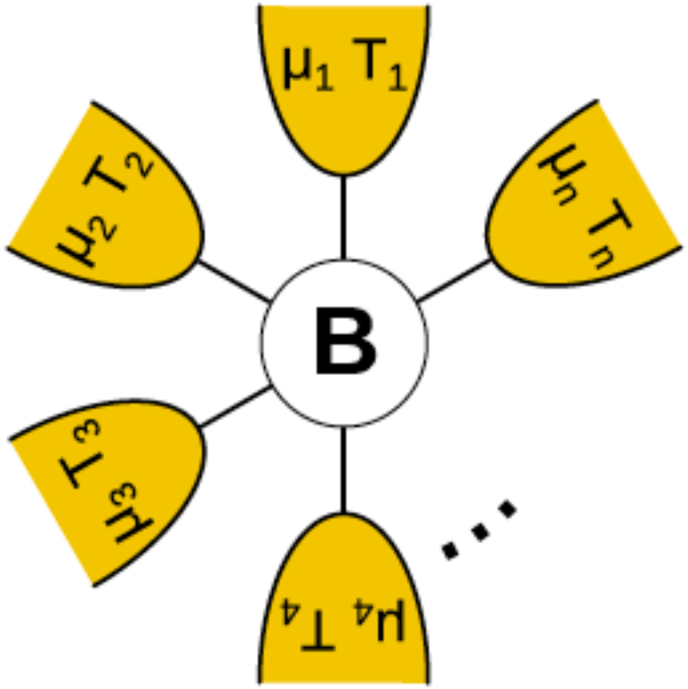
Bounds obtained for non-interacting 3-terminal transport

(K. Brandner, K. Saito, U. Seifert, PRL **110**, 070603 (2013))



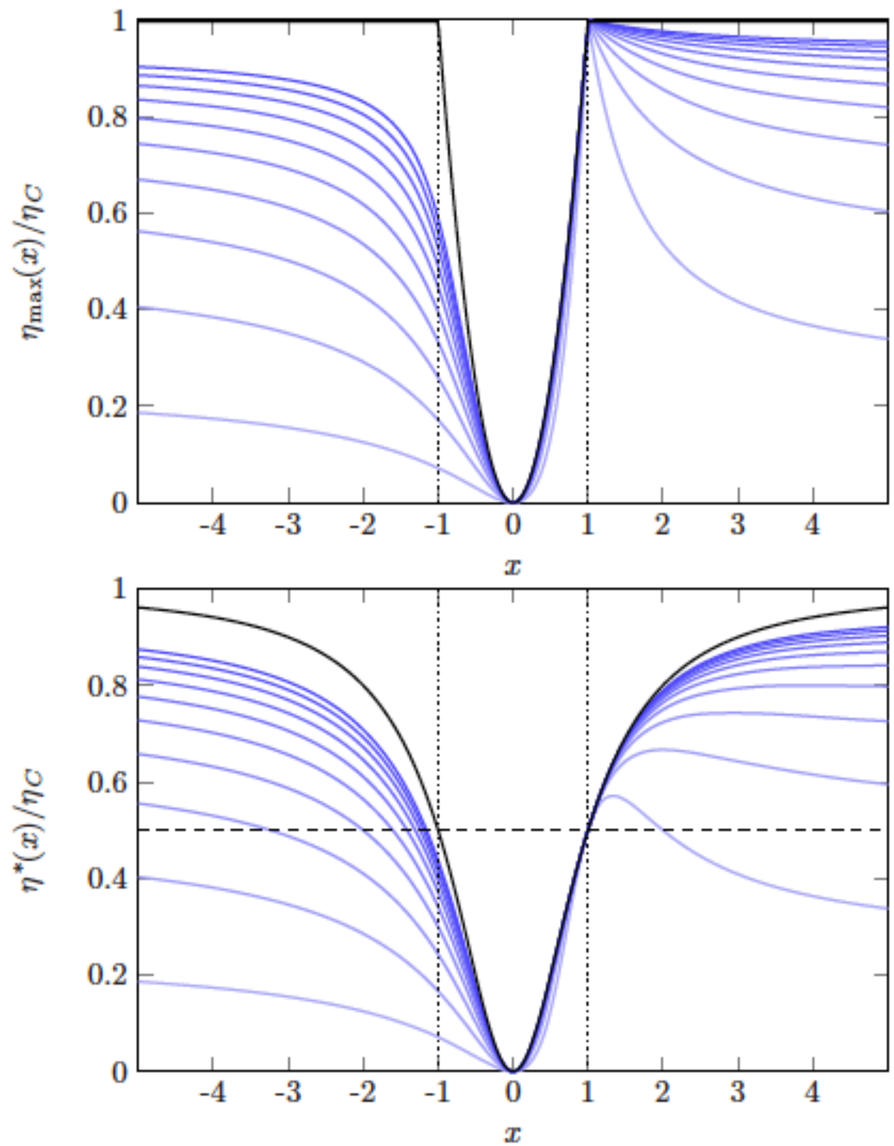
$$\eta(P_{\max}) = \frac{4}{7}\eta_C \quad \text{at} \quad x = \frac{4}{3}$$

Bounds for multi-terminal thermoelectricity



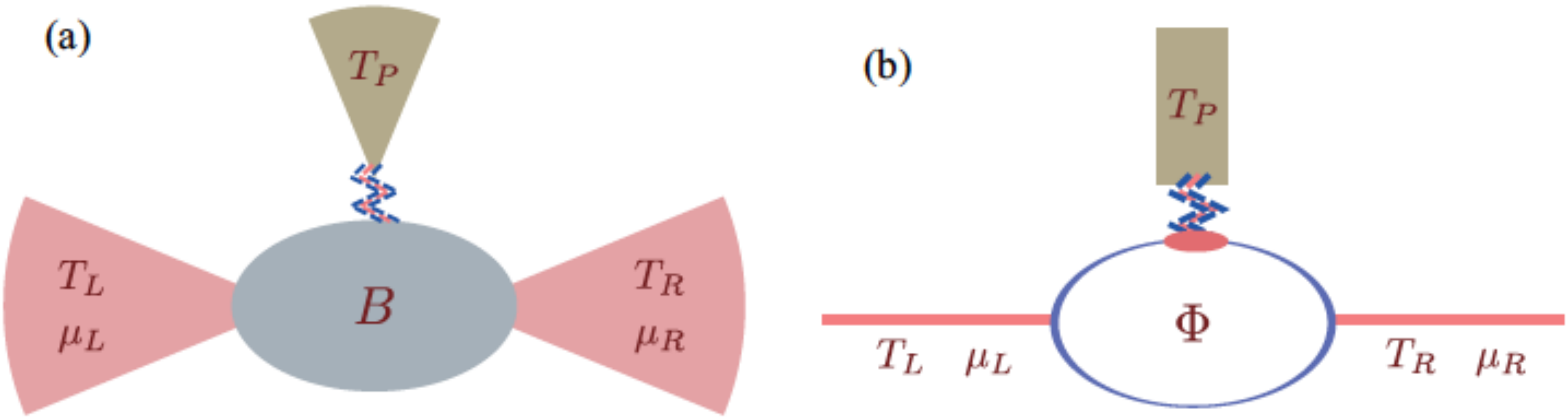
Numerical evidence that the power vanishes when the Carnot efficiency is approached

$n = 3, \ldots, 12$ terminals



[Brandner and Seifert, NJP **15**, 105003 (2013); PRE **91**, 012121 (2015)]

Bounds with electron-phonon scattering



Efficiency bounded by the non-negativity of the entropy production of the original three-terminal junction. However, the efficiency at maximum power can be enhanced

[Yamamoto, Entin-Wohlman, Aharony, Hatano; PRB **94**, 121402(R) (2015)]

Onsager-Casimir relations

Onsager reciprocal relations reflect at the macroscopic level the time-reversal symmetry of the microscopic dynamics, invariant under the transformation:

$$\mathcal{T}(\boldsymbol{r},\boldsymbol{p},t) \equiv (\boldsymbol{r},-\boldsymbol{p},-t) \quad \Rightarrow \quad L_{jk} = L_{kj}$$

With an applied magnetic field one instead obtains Onsager-Casimir relations:

$$\mathcal{T}_{\boldsymbol{B}}(\boldsymbol{r},\boldsymbol{p},t,\boldsymbol{B}) \equiv (\boldsymbol{r},-\boldsymbol{p},-t,-\boldsymbol{B}) \quad \Rightarrow \quad L_{jk}(\boldsymbol{B}) = L_{kj}(-\boldsymbol{B})$$

but in principle one could violate the Onsager symmetry: $L_{jk}(\boldsymbol{B}) \neq L_{kj}(\boldsymbol{B})$

Onsager relations and thermodynamic constraints on heat-to-work conversion

For thermoelectricity:

$$\Pi(\boldsymbol{B}) \neq TS(\boldsymbol{B}) \text{ [that is, } L_{eh}(\boldsymbol{B}) \neq L_{he}(\boldsymbol{B})]$$

and in principle one could have the Carnot efficiency at finite power:

$$P = \frac{\eta_C}{4} \frac{|L_{eh}^2 - L_{he}^2|}{L_{ee}} \mathcal{F}_h$$

Onsager relations
with broken time-reversal symmetry

Onsager relations under an applied magnetic field remain valid:

1) for noninteracting systems

2) if the magnetic field is constant

[Bonella, Ciccotti, Rondoni, EPL **108**, 60004 (2014)]

What about for a generic, spatially dependent magnetic field?

Symmetry without magnetic field inversion

$$H = \sum_{i}^{N} \frac{[\boldsymbol{p}_i - q_i \boldsymbol{A}(\boldsymbol{r}_i)]^2}{2m_i} + \frac{1}{2} \sum_{i \neq j} V(r_{ij})$$

Analytical result for $\boldsymbol{B} = B(x)\,\boldsymbol{k}$

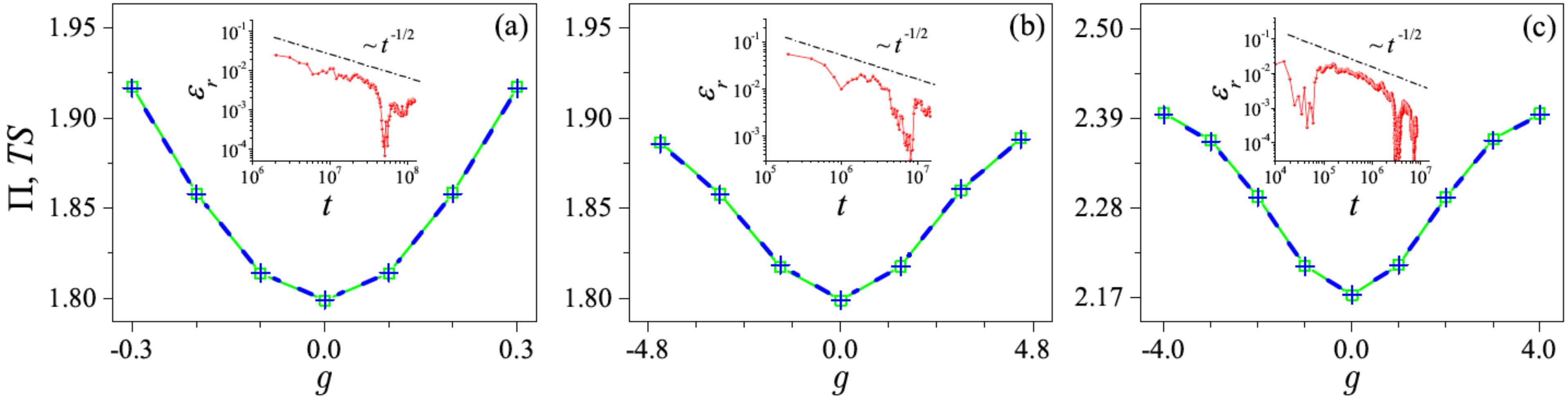
Landau gauge: $A(x)\,\boldsymbol{j}$

$$\begin{cases} \dot{x}_i = \dfrac{p_i^x}{m_i}, \\ \dot{y}_i = \dfrac{1}{m_i}\,[p_i^y - q_i A(x_i)], \\ \dot{z}_i = \dfrac{p_i^z}{m_i}, \\ \dot{p}_i^x = F_i^x + \dfrac{q_i}{m_i}\,[p_i^y - q_i A(x_i)]\,B(x_i), \\ \dot{p}_i^y = F_i^y, \\ \dot{p}_i^z = F_i^z, \end{cases} \qquad F_i^\alpha = -\frac{\partial \sum_{j \neq i} V(r_{ij})}{\partial \alpha}$$

Equations of motion invariant under:

$$\mathcal{M}(x, y, z, p^x, p^y, p^z, t, \boldsymbol{B}) \equiv (x, -y, z, -p^x, p^y, -p^z, -t, \boldsymbol{B})$$

Numerical results



$$B(x) = gx$$

generic 2D case:

$$B(x,y) = g\sin[\pi x/(2L)]\sin[\pi y/(2W)]$$

Theoretical argument:
divide the system into small volumes dV_α

Time-reversal trajectories without reversing the field for $dV_\alpha \to 0$

generic 3D case:

$$\boldsymbol{B} = g(B_x, B_y, B_z),$$
$$B_x = f_y f_z,\ B_y = f_z f_x,\ B_z = f_x f_y,$$
$$f_x = \sin[\pi x/(2L)],\ f_y = \sin[\pi y/(2W)],$$
$$f_z = \sin[\pi z/(2H)]$$

No-go theorem for finite power at the Carnot efficiency on purely thermodynamic grounds?

According to Nico Van Kampen Onsager derived his reciprocal relations in a *"stroke of genius"*

Onsager reciprocal relations much more general than expected so far.

Some open problems

Investigate strongly-interacting systems close to electronic phase transitions

In nonlinear regimes restrictions due to Onsager reciprocity relations might be overcome; useful for thermoelectricity?

Further investigate/optimize time-dependent driving

Power-efficiency-fluctuation trade-off for non-Markovian quantum dynamics?