Fundamental Aspects of Thermoelectricity

Giuliano Benenti
Center for Nonlinear and Complex Systems,
Univ. Insubria, Como, Italy
INFN, Milano, Italy

Ref.: G.B., G. Casati, K. Saito, R. Whitney, preprint arXiv:1608.05595

OUTLINE

I: Basic irreversible thermodynamics for coupled flows

II: Thermodynamic efficiency of steady-state thermal machines

III: Landauer theory for thermoelectric responses

IV: Aspects of thermoelectricity in interacting systems

V: Thermodynamic efficiency of cyclic thermal machines

Volta and the discovery of thermoelectricity

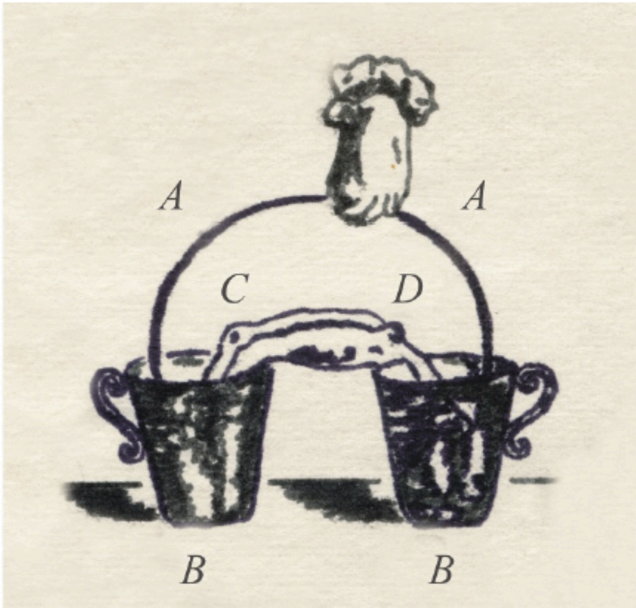


Fig. 3 Schematic of Volta's experiment that resulted in the discovery of thermoelectricity: A – metal (iron) arc; B – glasses with water; C and D – frog parts placed in the glasses with water.

(see Anatychuk et al, "On the discovery of thermoelectricity by A.Volta")

1794-1795: letters from Volta to Vassali. "*I immersed for some half-minute the end of such (iron) arc into boiling water and, without letting it to cool down, returned to experiments with two glasses of cold water. And it was then that the frog in water started contracting...*"

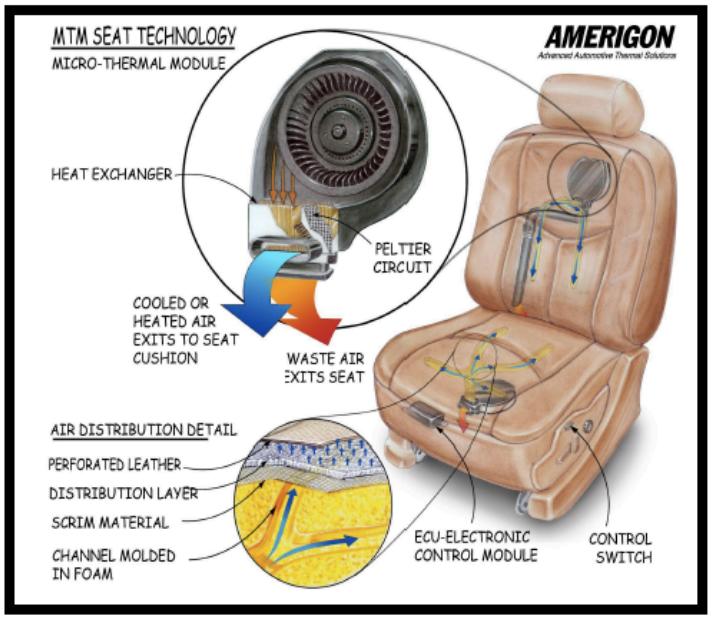
Abram Ioffe (1950s): Doped semiconductors have large thermoelectric effect

The initial excitement about semiconductors in the 1950s was due to their promise, not in electronics but in refrigeration. The goal was to build environmental benign solid state home refrigerators and power generators

Thermoelectric (Peltier) refrigerators have poor efficiency compared to compressor-based refrigerators

Niche applications: space missions, medical applications, laboratory equipments, air conditioning in submarines (reliability and quiet operation more important than cost)

car's seats cooler/heater



Use vehicle waste heat to improve fuel economy

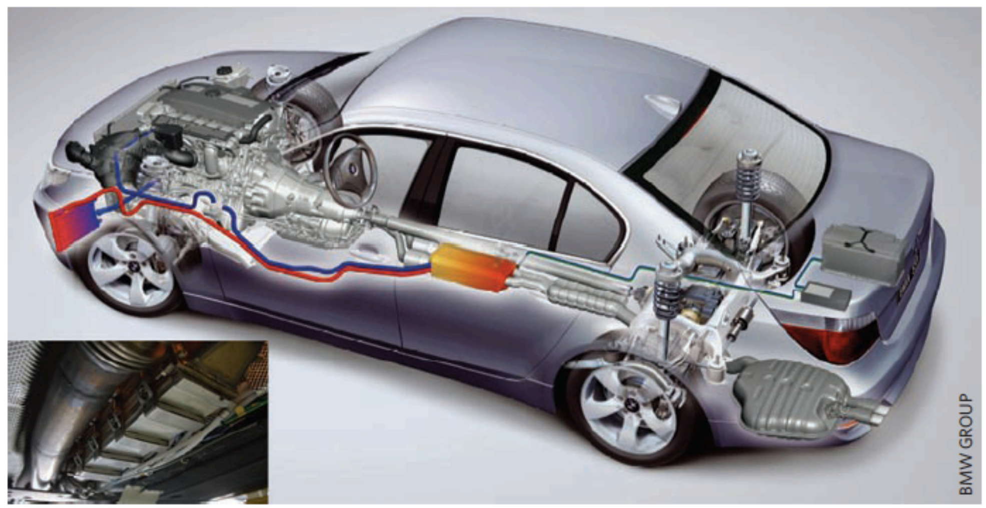


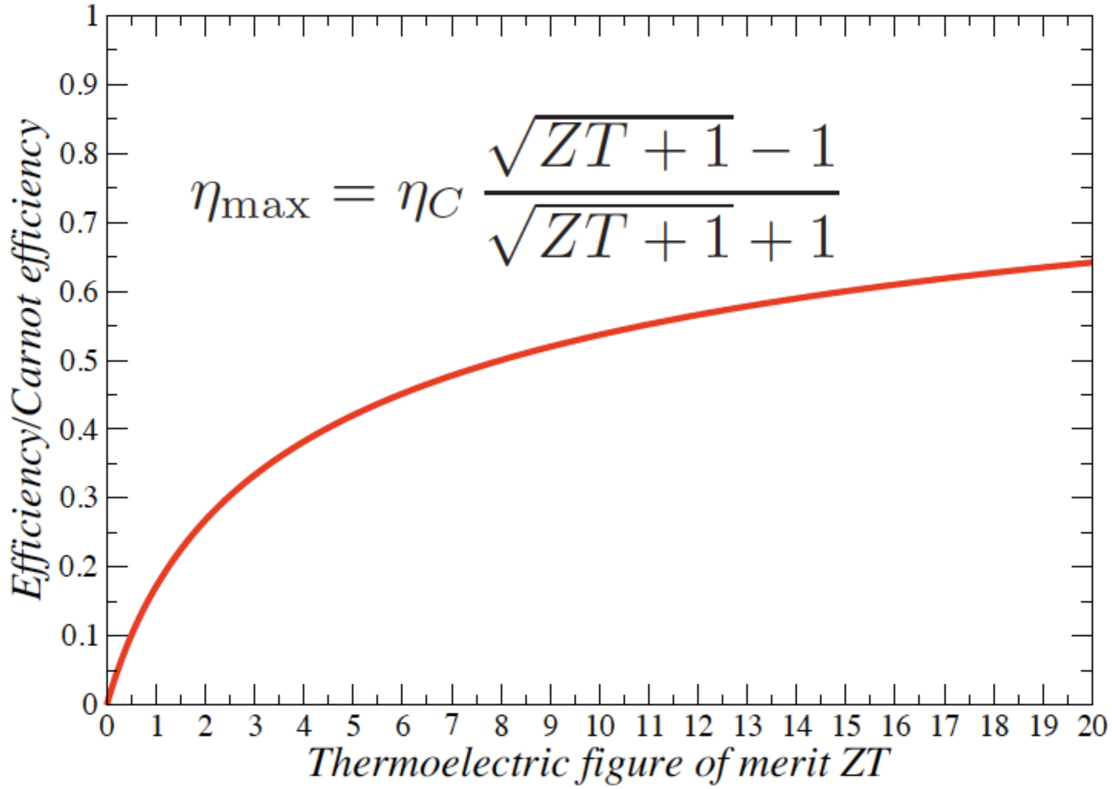
Figure 1 | Integrating thermoelectrics into vehicles for improved fuel efficiency. Shown is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue).

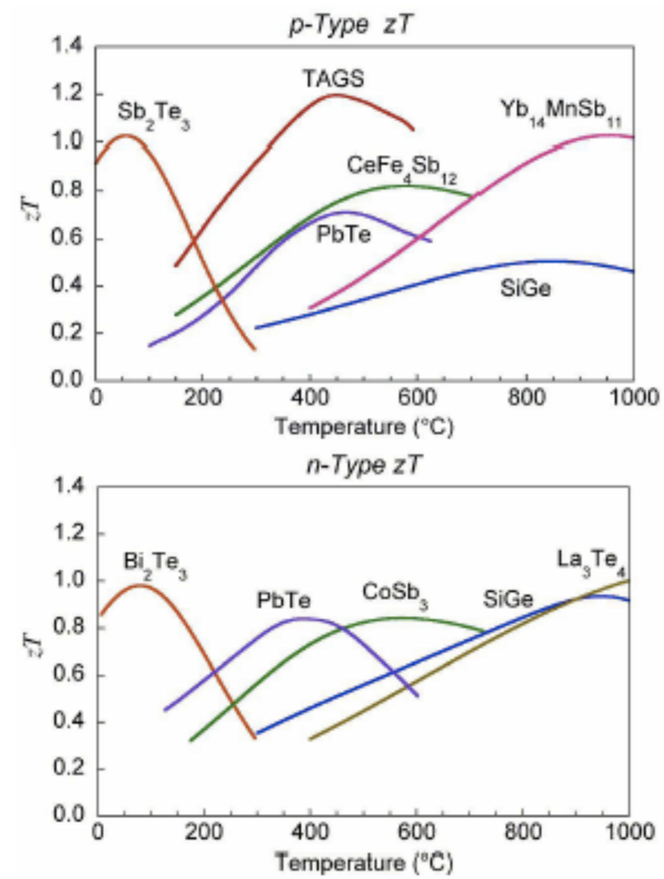
Mildred Dresselhaus et al. (Adv. Materials, 2007):

"a newly emerging field of low-dimensional thermoelectricity, enabled by material nanoscience and nanotechnology... Thermoelectric phenomena are expected to play an increasingly important role in meeting the energy challenge for the future..."

Small scale thermoelectricity could be relevant for cooling directly on chip, by purely electronic means. Nanoscale heat management is crucial to reduce the energy cost in many applications of microelectronics.

Thermoelectric applications are limited due to the low conversion efficiency





Cronin Vining: *limited role for thermoelectrics in the climate crisis (ZT too small to replace mechanical engines for large-scale applications)*
Arun Majumdar: at issue are some fundamental scientific challenges, which could be overcome by deeper understanding of charge and heat transport...

Irreversible thermodynamic

Irreversible thermodynamics based on the postulates of equilibrium thermostatics plus the postulate of time-reversal symmetry of physical laws (if time t is replaced by $-t$ and simultaneously applied magnetic field $\boldsymbol{B}$ by $-\boldsymbol{B}$)

The thermodynamic theory of irreversible processes is based on the Onsager Reciprocity Theorem

Refs.: H. B. Callen, Thermodynamics and an introduction to thermostatics
S. R. de Groot and P. Mazur, Non-equilibrium thermodynamics

Thermodynamic forces and fluxes

Irreversible processes are driven by thermodynamic forces (or generalized forces or affinities) $\mathcal{F}_k$

Fluxes J_i characterize the response of the system to the applied forces

Entropy production rate given by the sum of the products of each flux with its associated thermodynamic force

$$\mathscr{S} = \mathscr{S}(U, V, N_1, N_2, \ldots) = \mathscr{S}(E_0, E_1, E_2, \ldots)$$

$$\frac{d\mathscr{S}}{dt} = \sum_k \frac{\partial \mathscr{S}}{\partial E_k} \frac{dE_k}{dt} = \sum_k \mathcal{F}_k J_k$$

Linear response

Purely resistive systems: fluxes at a given instant depend only on the thermodynamic forces at that instant (memory effects not considered)

$$J_i = \sum_j L_{ij}\mathcal{F}_j + \sum_{j,k} L_{ijk}\mathcal{F}_j\mathcal{F}_k + \ldots$$

Fluxes vanish as thermodynamic forces vanish

Linear (and purely resistive) processes:

$$J_i = \sum_j L_{ij}\mathcal{F}_j$$

L_{ij} Onsager coefficients (first-order kinetic coefficients) depend on intensive quantities (T,P,μ,...)

Phenomenological linear Ohm's, Fourier's, Fick's laws

Onsager-Casimir reciprocal relations

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

Relationship of Onsager theorem to time-reversal symmetry of physical laws

Consider delayed correlation moments of fluctuations (for simplicity without applied magnetic fields)

$$\delta E_j(t) \equiv E_j(t) - E_j, \quad \langle \delta E_j \rangle = 0,$$

$$\langle \delta E_j(t) \delta E_k(t+\tau) \rangle = \langle \delta E_j(t) \delta E_k(t-\tau) \rangle = \langle \delta E_j(t+\tau) \delta E_k(t) \rangle$$

$$\lim_{\tau \to 0} \left\langle \delta E_j(t) \frac{\delta E_k(t+\tau) - \delta E_k(t)}{\tau} \right\rangle = \lim_{\tau \to 0} \left\langle \frac{\delta E_j(t+\tau) - \delta E_j(t)}{\tau} \delta E_k(t) \right\rangle$$

$$\langle \delta E_j \delta \dot{E}_k \rangle = \langle \delta \dot{E}_j \delta E_k \rangle$$

Assume that fluctuations decay is governed by the same linear dynamical laws as are macroscopic processes

$$\delta \dot{E}_k = \sum_l L_{kl} \delta \mathcal{F}_l$$

$$\sum_l L_{kl} \langle \delta E_j \delta \mathcal{F}_l \rangle = \sum_j L_{jl} \langle \delta \mathcal{F}_l \delta E_k \rangle$$

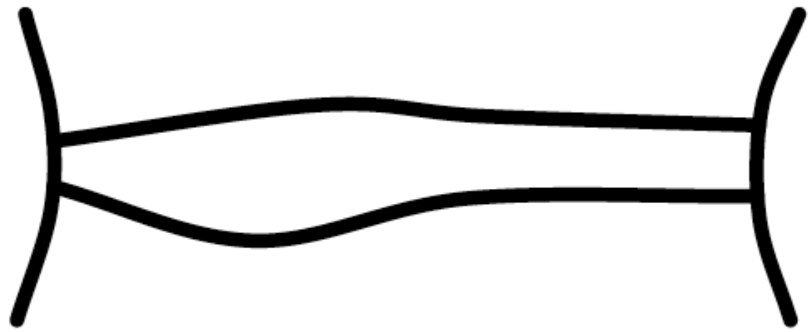
Assume that the fluctuation of each thermodynamic force is associated only with the fluctuation of the corresponding extensive variable

$$\langle \delta E_j \delta \mathcal{F}_l \rangle = 0 \;\; \text{if} \;\; j \neq l$$

Coupled 1D particle and heat transport

Stochastic baths: ideal gases at fixed temperature and electrochemical potential

T_L μ_L



T_R μ_R

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

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

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

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

$$\Delta T = T_L - T_R$$

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

Restrictions from thermodynamics

Entropy production rate:

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

Positivity of entropy production:

$$L_{ee} \geq 0, \quad L_{hh} \geq 0, \quad L_{ee}L_{hh} - \frac{1}{4}(L_{eh} + L_{he})^2 \geq 0$$

Onsager-Casimir relations:

$$L_{ab}(\boldsymbol{B}) = L_{ba}(-\boldsymbol{B})$$

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)

Heat dissipation rate

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

Joule heating

heat lost by
thermal resistance

disappears for time-reversal
symmetric systems

To minimize
dissipation large G and
small K are needed

Local equilibrium

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

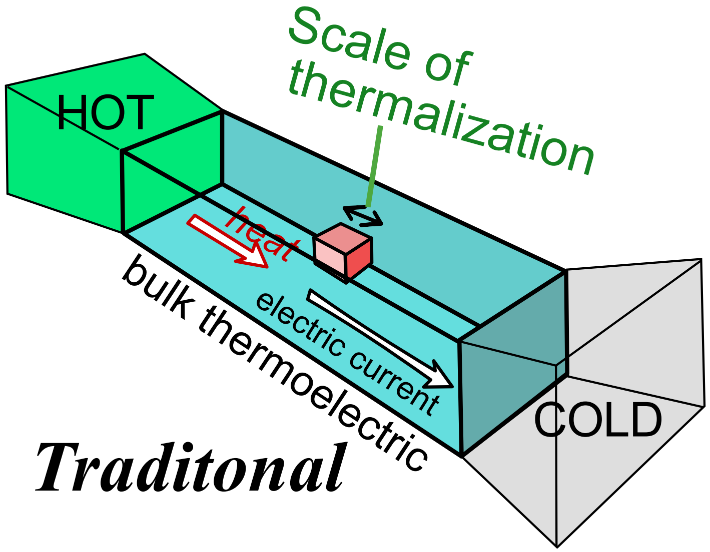
$$\begin{cases} j_e = \lambda_{ee}(-\nabla\mu/eT) + \lambda_{eh}\nabla(1/T), \\ \\ j_h = \lambda_{he}(-\nabla\mu/eT) + \lambda_{hh}\nabla(1/T) \end{cases}$$

j_e, j_h charge and heat current densities

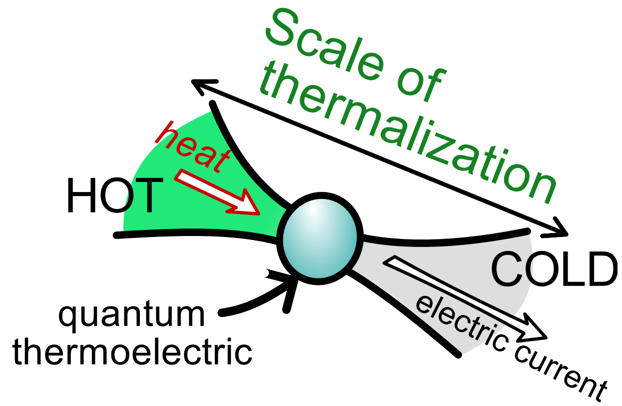
In this case we connect Onsager coefficients to electric and thermal conductivity rather than to conductances

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

Traditional versus quantum thermoelectrics



Traditonal



Quantum

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

Linear response?

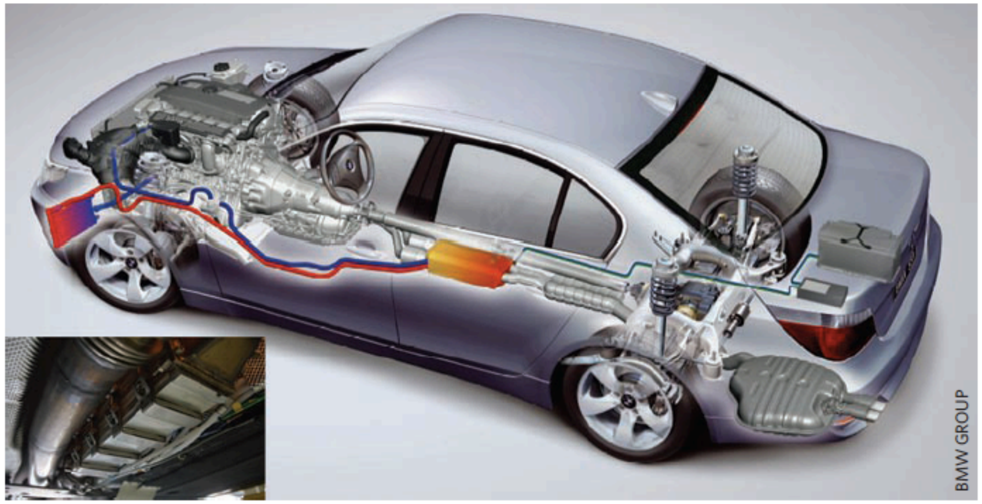


Figure 1 | Integrating thermoelectrics into vehicles for improved fuel efficiency. Shown is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue).

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

(exhaust gases)

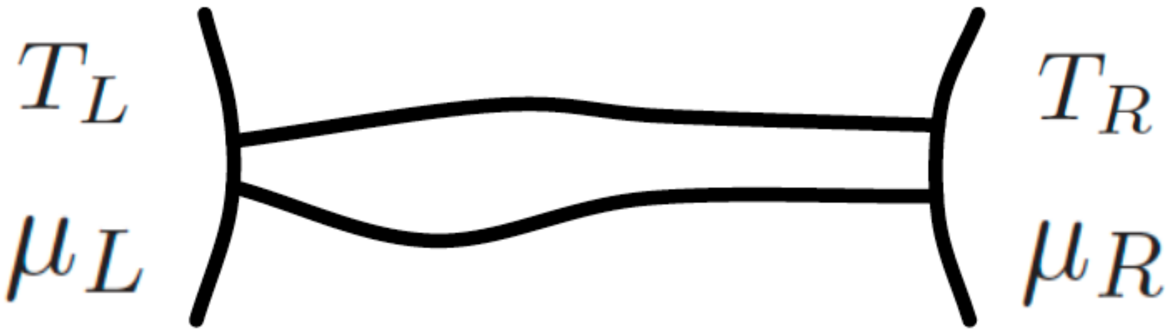
$$T_C \sim 270 - 300\,\mathrm{K}$$

(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)

Heat and energy representations



$$J_h = J_u - \mu J_\rho = J_u - (\mu/e) J_e$$

$$\begin{cases} J_e = L_{ee}\mathfrak{F}_e + L_{eh}\mathfrak{F}_h \\ \\ J_h = L_{he}\mathfrak{F}_e + L_{hh}\mathfrak{F}_h \end{cases} \qquad \begin{cases} J_e = \tilde{L}_{ee}\tilde{\mathfrak{F}}_e + \tilde{L}_{eu}\tilde{\mathfrak{F}}_u \\ \\ J_u = \tilde{L}_{ue}\tilde{\mathfrak{F}}_e + \tilde{L}_{uu}\tilde{\mathfrak{F}}_e \end{cases}$$

$$\mathfrak{F}_e = \Delta V/T \qquad \tilde{\mathfrak{F}}_e = \Delta(V/T) = \mathfrak{F}_e - (\mu/e)\mathfrak{F}_h$$

$$\mathfrak{F}_h = \Delta T/T^2 \qquad \tilde{\mathfrak{F}}_u = \mathfrak{F}_h$$

$$\dot{\mathscr{S}} = \mathfrak{F}_e J_e + \mathfrak{F}_h J_h \qquad \dot{\mathscr{S}} = \tilde{\mathfrak{F}}_e J_e + \tilde{\mathfrak{F}}_u J_u$$

Carnot efficiency

$$\eta = \frac{W}{Q_L} \leq \eta_C = 1 - \frac{T_R}{T_L} \qquad (T_L > T_R)$$

The ideal Carnot efficiency may be achieved in the limit of quasi-static (reversible) processes, so that the extracted power reduces to zero.

Time-reversal symmetric systems

Onsager reciprocal relations:

$$L_{eh} = L_{he} \qquad (\Pi = TS)$$

Positivity of entropy production:

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

Maximum efficiency

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

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

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

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

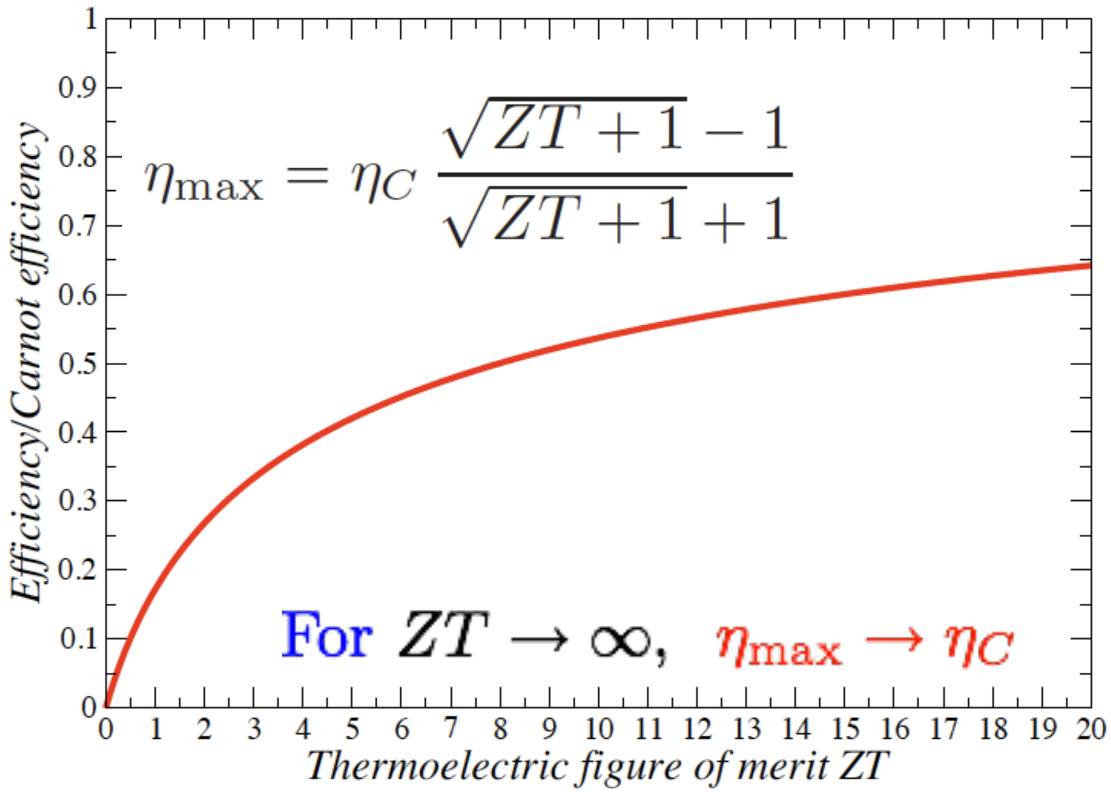
Maximum efficiency (for system with time-reversal symmetry)

$$\eta_{\max} = \eta_C \frac{\sqrt{ZT+1} - 1}{\sqrt{ZT+1} + 1}$$

Thermoelectric figure of merit

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

Positivity of entropy production implies $ZT > 0$



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:

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

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

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

Finite time thermodynamics

In an ideal Carnot engine conversion processes are quasi-static and the extracted power reduces to zero.

How much the efficiency deteriorates when heat to work conversion takes place in a finite time?

Finite time thermodynamics: finite-time steady-state conversion processes or thermodynamic cycles; the efficiency at the maximum output power is an important concept

Ref.: B. Andresen, Angew. Chem. Int. Ed. 50 (2011) 2690

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 $\mathfrak{F}_e = -\frac{L_{eh}}{2L_{ee}}\mathfrak{F}_h$

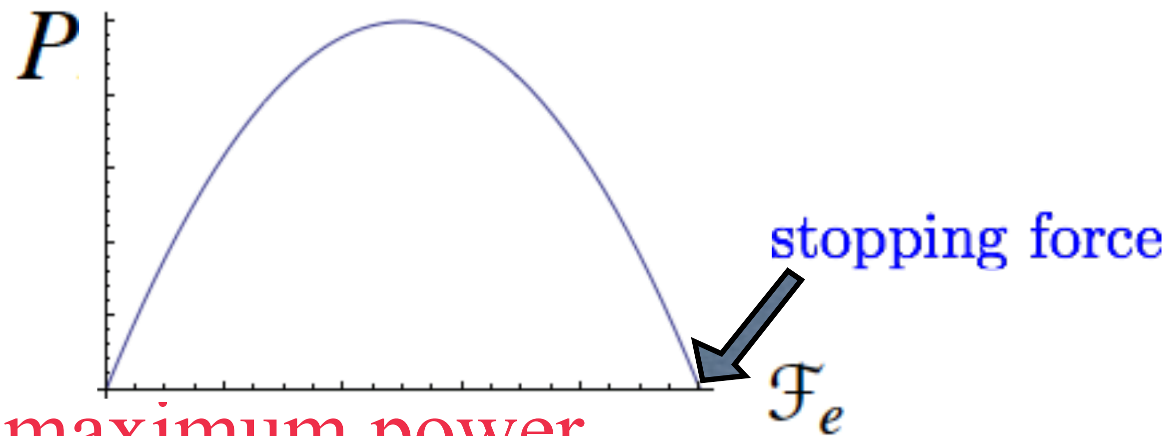
Maximum output power

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

Power factor S^2G

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

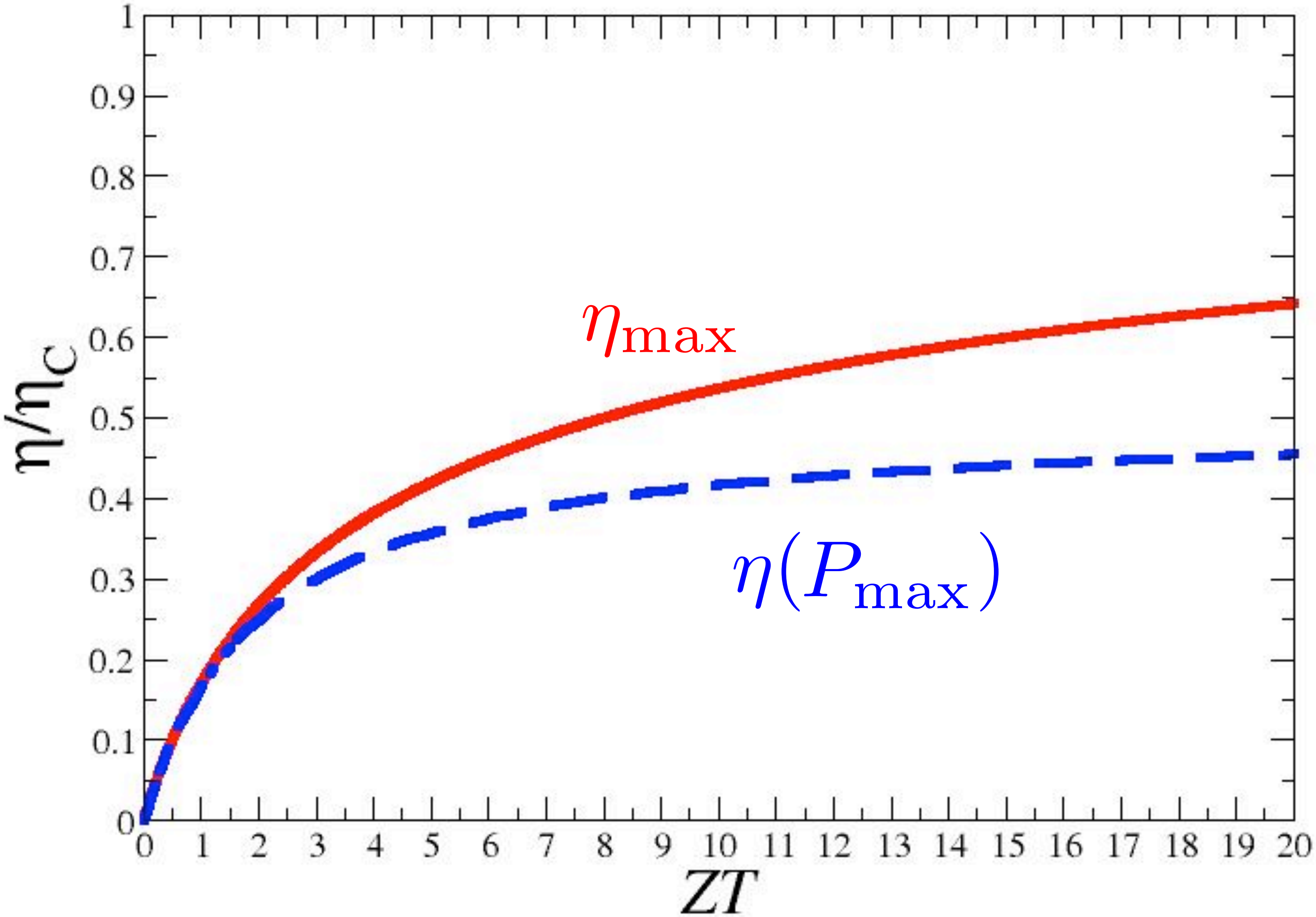
$$\mathcal{F}_e^{\text{stop}} = -\frac{L_{eh}}{L_{ee}}\mathcal{F}_h, \qquad J_e(\mathcal{F}_e^{\text{stop}}) = 0$$



Efficiency at maximum power

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

η_{CA} Curzon-Ahlborn upper bound

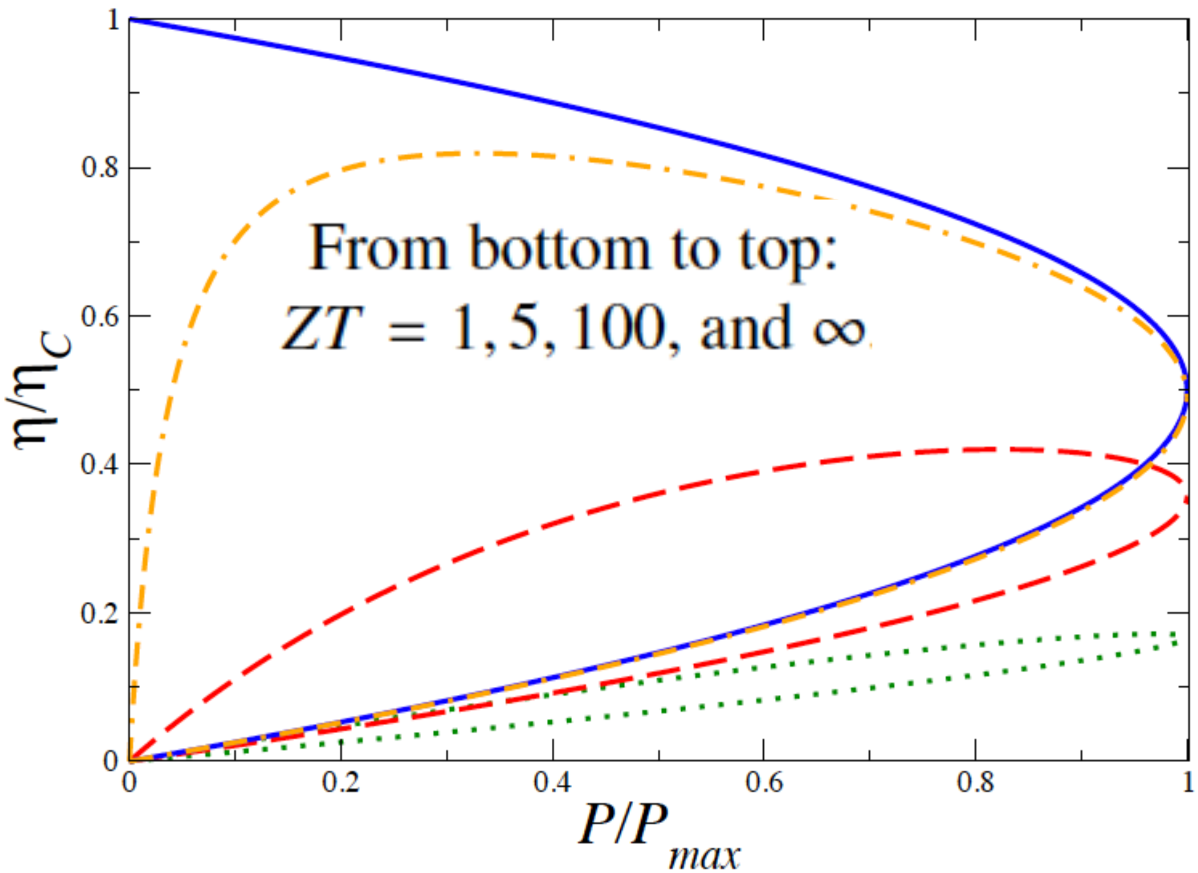


1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
η/η_C
$\eta_{\max}$
$\eta(P_{\max})$
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
ZT

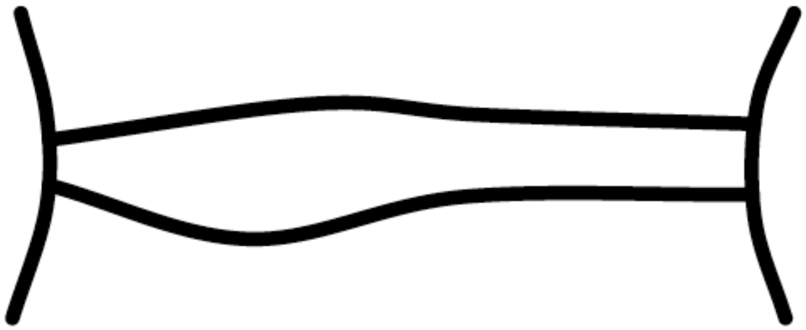
Efficiency versus power

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

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



Maximum refrigeration efficiency



$(T_L > T_R)$

Cooling power J_h (heat extracted from the cold reservoir)

Coefficient of performance (COP)

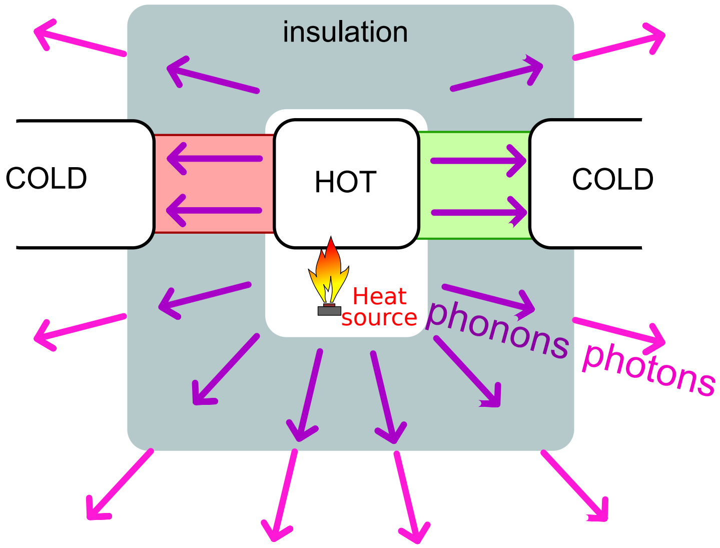
$$\eta^{(r)} = \frac{J_h}{P} \qquad (J_h < 0,\ P < 0)$$

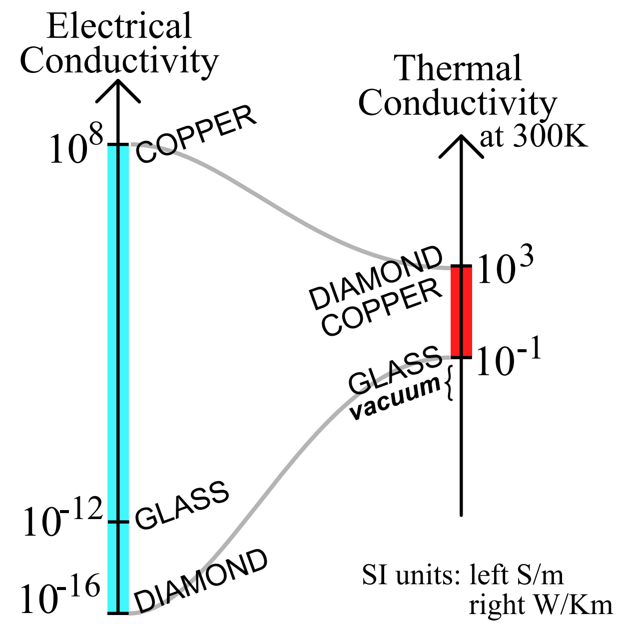
$$\eta^{(r)}_{\max} = \eta^{(r)}_C \frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+1}, \qquad \eta^{(r)}_C = T_R/(T_L - T_R)$$

(can be >1)

ZT is the figure of merit also for refrigeration

Phonons (and photons) as detrimental effects





The heat carried away from the heat source by phonons (and photons) cannot contribute to power production

$$\eta = \frac{P}{J_h^{(\mathrm{ph})} + J_h^{(\mathrm{el})}} = \frac{P}{J_h^{(\mathrm{el})}} \frac{J_h^{(\mathrm{el})}}{J_h^{(\mathrm{ph})} + J_h^{(\mathrm{el})}} \leq \eta_C \frac{J_h^{(\mathrm{el})}}{J_h^{(\mathrm{ph})} + J_h^{(\mathrm{el})}}$$

Reducing thermal conductivity

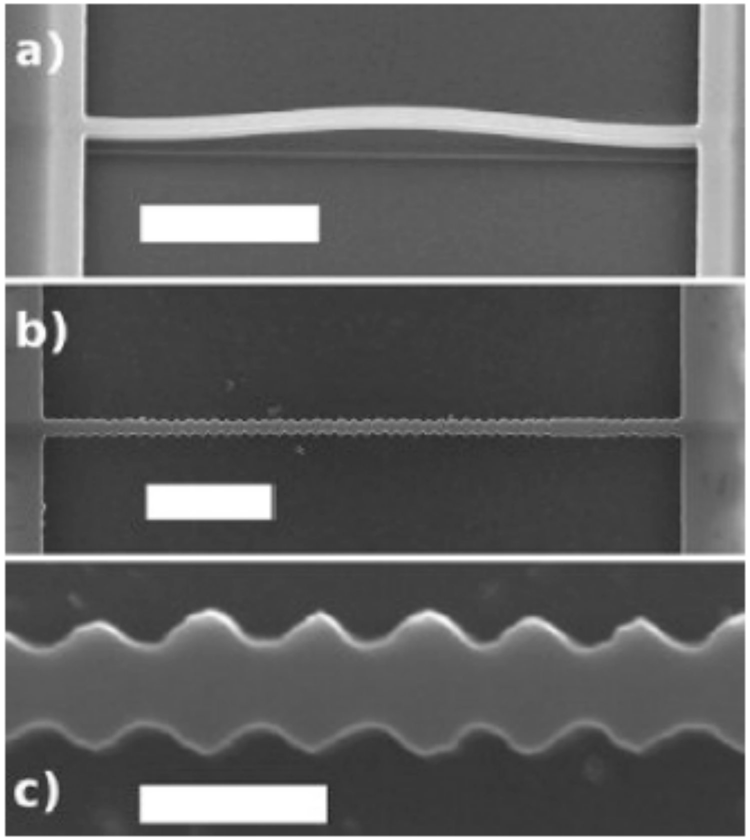


FIG. 1. SEM images of the straight (a) and the corrugated (b) nanowires; (c) corresponds to the top view of the corrugated nanowire. The scale bars correspond to (a) 2 μm, (b) 2 μm, and (c) 300 nm.

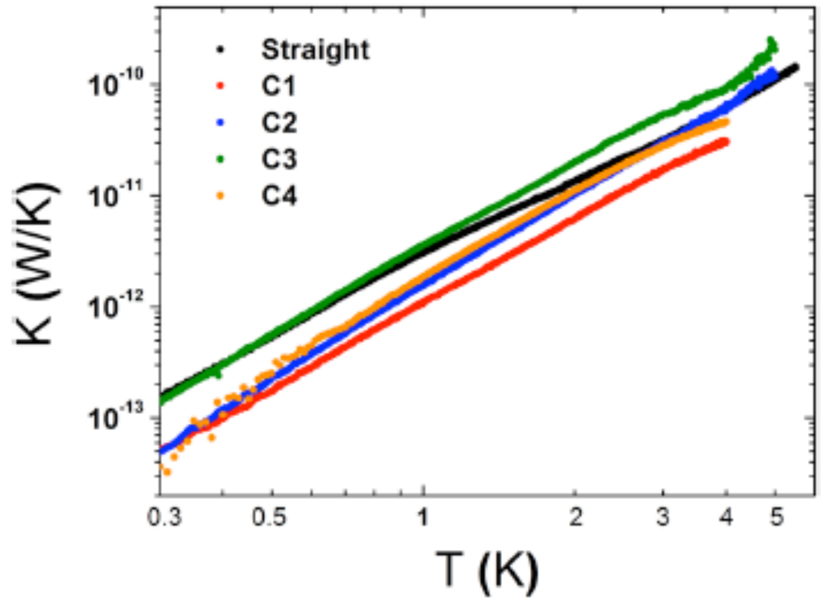


FIG. 2. Thermal conductance versus temperature for a straight nanowire and four corrugated nanowires in the log-log scale.

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

Conditions for Carnot efficiency

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

$$\mathrm{cond}(\boldsymbol{L}) \equiv \frac{[\mathrm{Tr}(\boldsymbol{L})]^2}{\det \boldsymbol{L}} > ZT$$

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

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)

Non-interacting systems, Landauer formalism

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:

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

$\tau(E)$ transmission probability for a particle with energy E

$f_\alpha(E)$ Fermi distribution of the particles injected from reservoir α

Thermoelectric efficiency

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

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

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

Delta-energy filtering mechanism

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

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

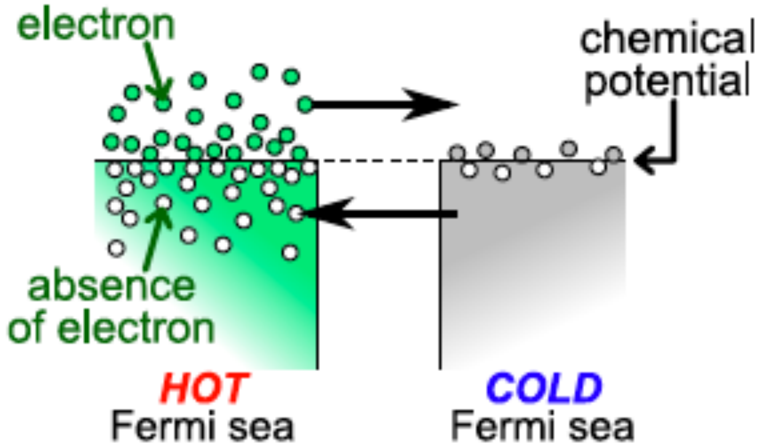
$$\eta = \eta_C = 1 - T_R/T_L$$ **Carnot efficiency**

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)]

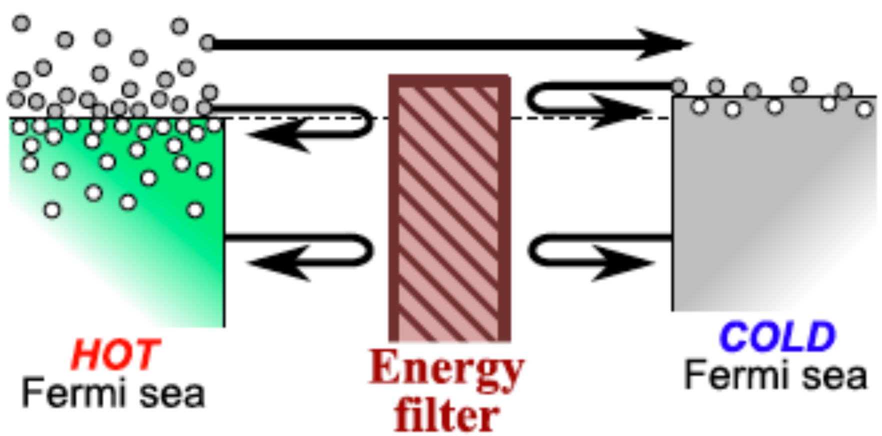
Heat-to-work conversion through energy filtering

(a) Direct contact - no energy filter

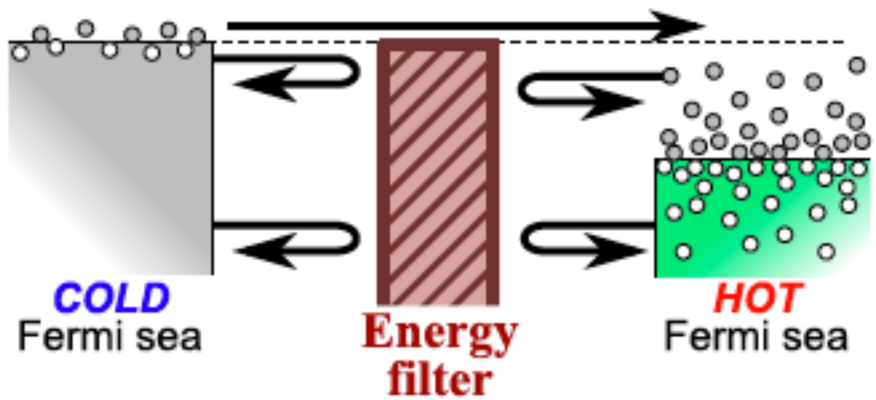


Flow of heat from hot to cold but no flow of charge

(b) Energy-filter as heat-engine



(c) Energy-filter as refrigerator



Linear response: Onsager coefficients

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 in macroscopic conductors is directly proportional to the temperature, with a proportionality factor which is to a good accuracy the same for all metals.

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

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

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

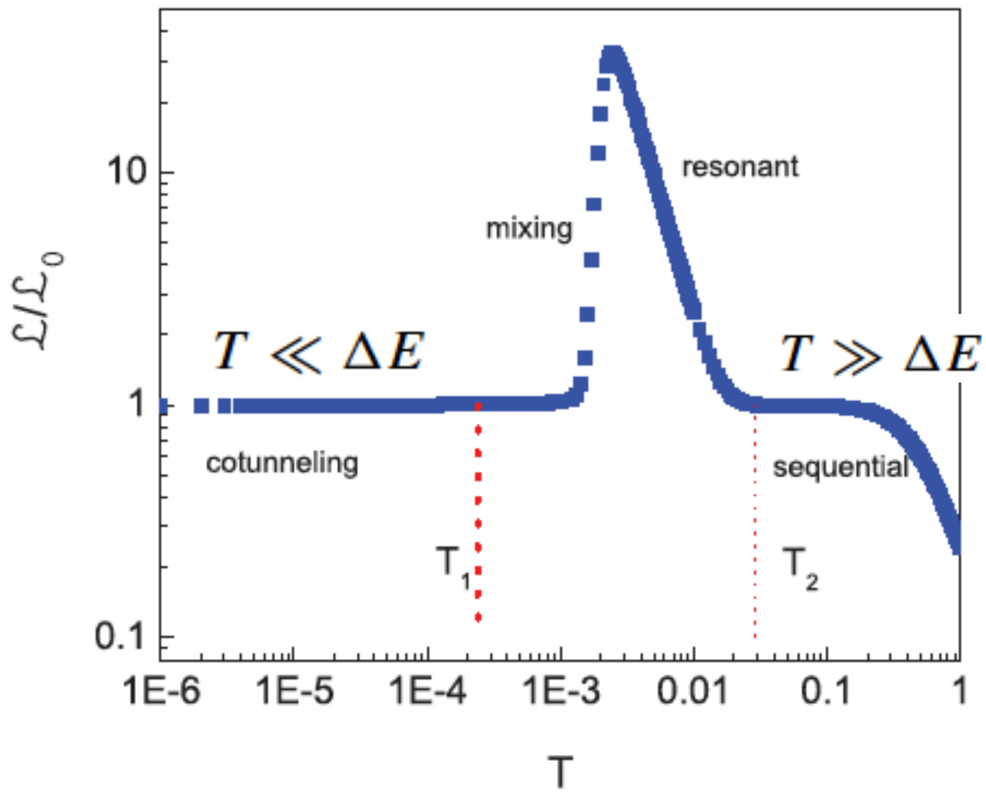
Wiedemann-Franz law derived under the condition $L_{ee}L_{hh}>>(L_{eh})^2$ and therefore

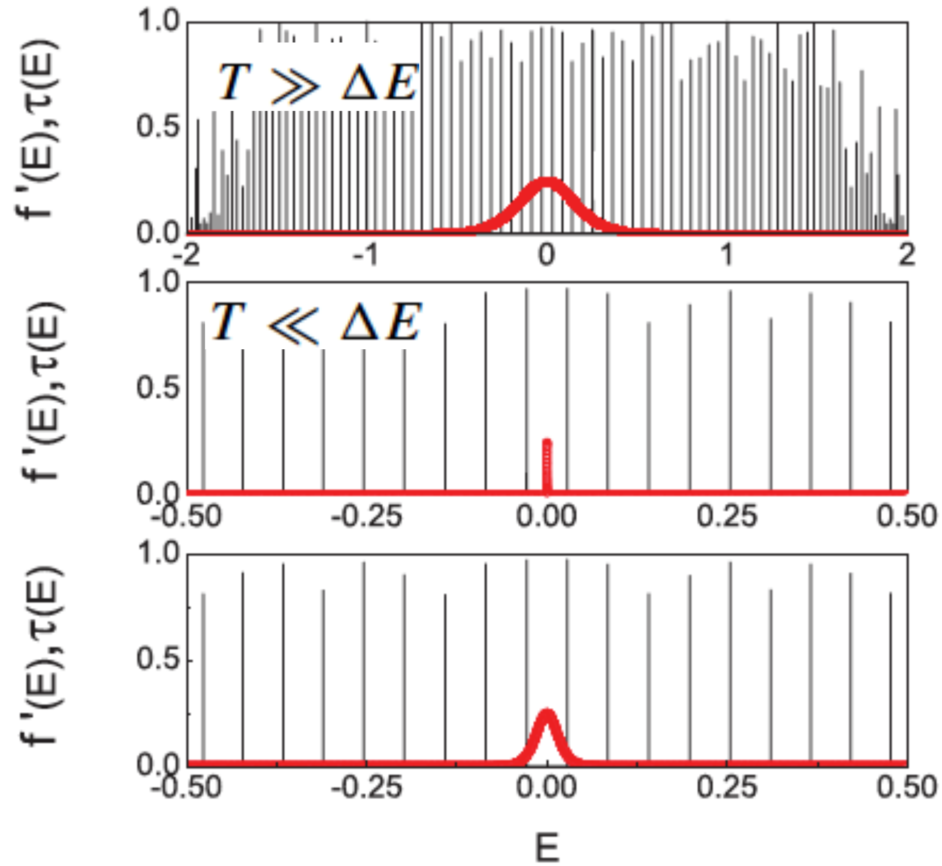
$$ZT = L_{eh}^2/\det \boldsymbol{L} \approx L_{eh}^2/L_{ee}L_{hh} \ll 1$$

Wiedemann-Franz law violated in

- low-dimensional interacting systems that exhibit non-Fermi liquid behavior
- small systems where transmission can show significant energy dependence

(Violation of) Wiedemann-Franz law in small systems





(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 $\tau(E) \approx \tau(\mu) + \tau'(\mu)(E-\mu)$

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

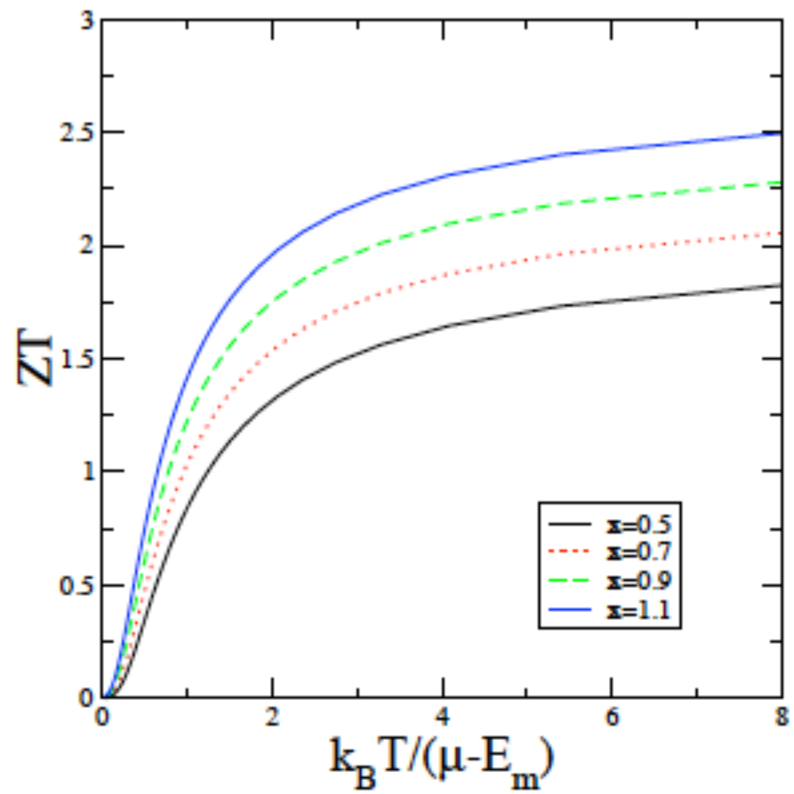
Electron and holes contribute with opposite signs: we want sharp, asymmetric transmission functions to have large thermopowers (ex: resonances, Anderson QPT, see Imry and Amir, 2010), violation of WF, large ZT.

Metal-insulator 3D Anderson transition

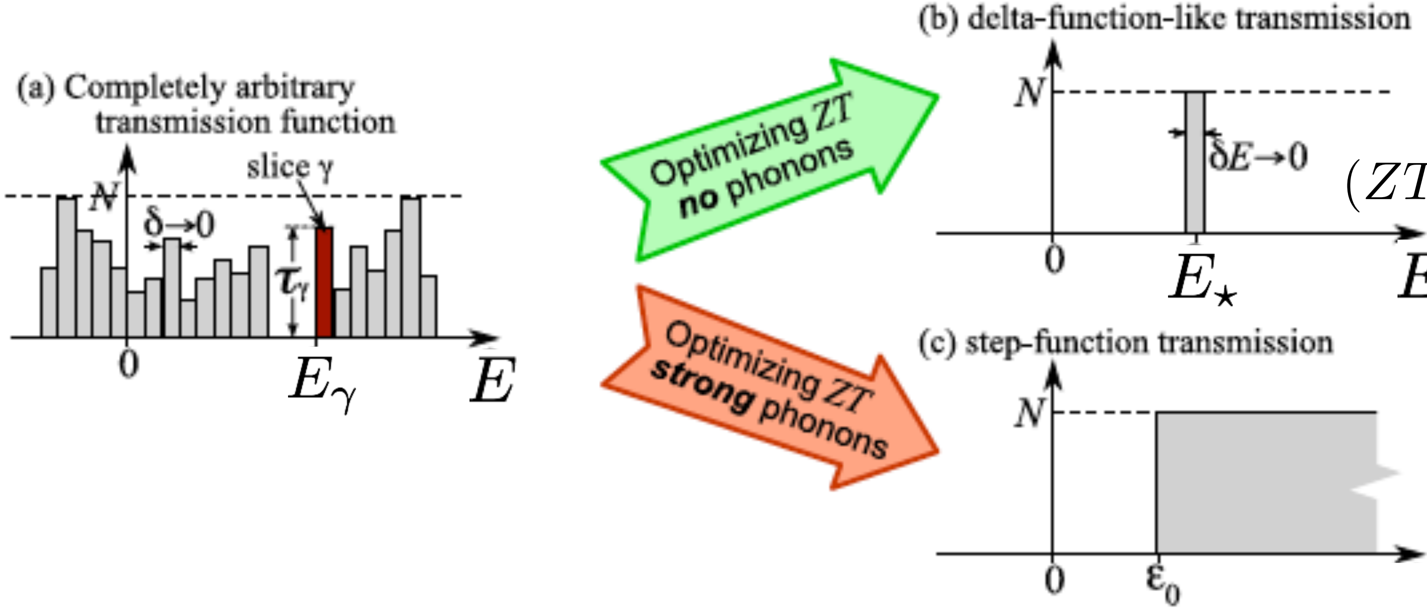
$$\sigma = \int_{-\infty}^{\infty} dE \sigma_0(E) \left(-\frac{\partial f}{\partial E} \right) \qquad \sigma_0(E) = \begin{cases} A(E - E_m)^x, & \text{if } E \geq E_m, \\ 0, & \text{if } E \leq E_m, \end{cases}$$

x conductivity critical exponent

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



Including phonons



$(ZT = 0 \text{ if } K_{\rm ph} \neq 0)$

Boxcar transmission function (band pass filter) optimum for intermediate phonon heat flows

[Whitney, PRL **112**, 130601 (2014)]

Calculation for $K_{ph} \gg K_{el}$

$$ZT \simeq \frac{GTS^2}{K_{\mathrm{ph}}} = \frac{1}{K_{\mathrm{ph}}T} I_0 \langle E \rangle^2$$

$$\mu = 0,$$
$$\langle E \rangle = I_1 / I_0$$

Transmission at high energies increases both I_0 and $\langle E \rangle$, thus enhancing ZT

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

$$\frac{\mathrm{d}I_n}{\mathrm{d}\tau_\gamma} = \frac{\delta}{h} E_\gamma^n \left(-f'(E_\gamma)\right)$$

$$\frac{d(ZT)}{d\tau_\gamma} = \frac{1}{K_{\mathrm{ph}}T}\left(\frac{2I_1}{I_0}\frac{dI_1}{d\tau_\gamma} - \frac{I_1^2}{I_0^2}\frac{dI_0}{d\tau_\gamma}\right) = -\frac{f'(E_\gamma)}{K_{\mathrm{ph}}T}\frac{\delta}{h}\langle E \rangle \left(2E_\gamma - \langle E \rangle\right)$$

Convenient to increase τ_γ for $E_\gamma > \frac{1}{2}\langle E \rangle$

Optimum transmission function is a step function.

For N modes: $\tau(E) = N\,\theta\,[E-\epsilon_0]\,, \quad 2\epsilon_0 = \langle E(\epsilon_0)\rangle$

$$\langle E(\epsilon_0)\rangle = \frac{\int_{\epsilon_0}^{\infty} \mathrm{d}E\, E\,(-f'(E))}{\int_{\epsilon_0}^{\infty} \mathrm{d}E\,(-f'(E))} = \epsilon_0 + \frac{k_\mathrm{B}T \ln[1+\exp[-\epsilon_0/(k_\mathrm{B}T)]]}{f(\epsilon_0)}$$

$$\frac{\epsilon_0}{k_\mathrm{B}T} f(\epsilon_0) = \ln[1+\exp[-\epsilon_0/(k_\mathrm{B}T)]]$$

$$ZT = \frac{1}{K_{\mathrm{ph}}T}\frac{N\epsilon_0^2 f(\epsilon_0)}{h} = \frac{k_B^2 T}{hK_{\mathrm{ph}}} N \times 0.317\ldots$$

$$K_\mathrm{el} \sim k_\mathrm{B}^2 T N/h \qquad\qquad ZT \sim \frac{K_\mathrm{el}}{K_\mathrm{ph}} \ll 1$$

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 N-mode constriction which lets particle flow at all energies:

$$J_{h,i}^{\max} = \frac{\pi^2}{6h} N\, k_B^2 T_i^2$$

Nernst's unattainability principle follows:

$$J_{h,i}^{\max} \propto T_i^2, \quad C_i \equiv (\bar{d}Q_i/\mathrm{d}T_i) \propto T_i \Rightarrow \qquad \frac{\mathrm{d}T_i}{\mathrm{d}t} \propto -T_i$$

Maximum power of a heat engine

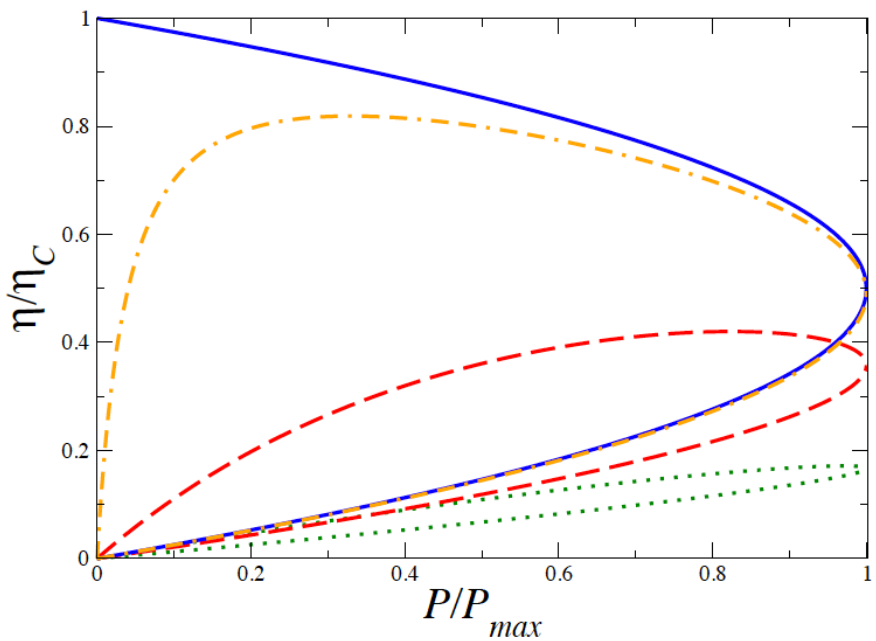
Since the heat flow must be less than the Bekenstein-Pendry bound and the efficiency smaller than Carnot efficiency also the output power must be bounded

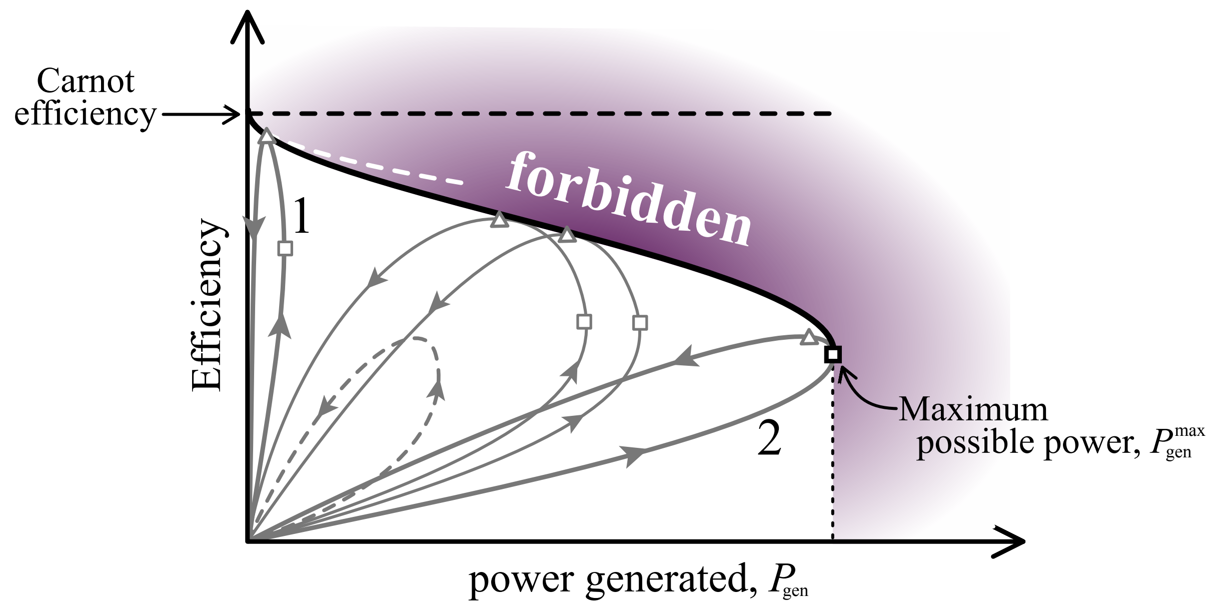
Within scattering theory:

$$P_{\mathrm{gen}}^{\mathrm{max}} \equiv A_0 \frac{\pi^2}{h} N\, k_{\mathrm{B}}^2 (T_L - T_R)^2, \quad A_0 \simeq 0.0321$$

[Whitney, PRL **112**, 130601 (2014)]

Trade-off between max. power and max. efficiency



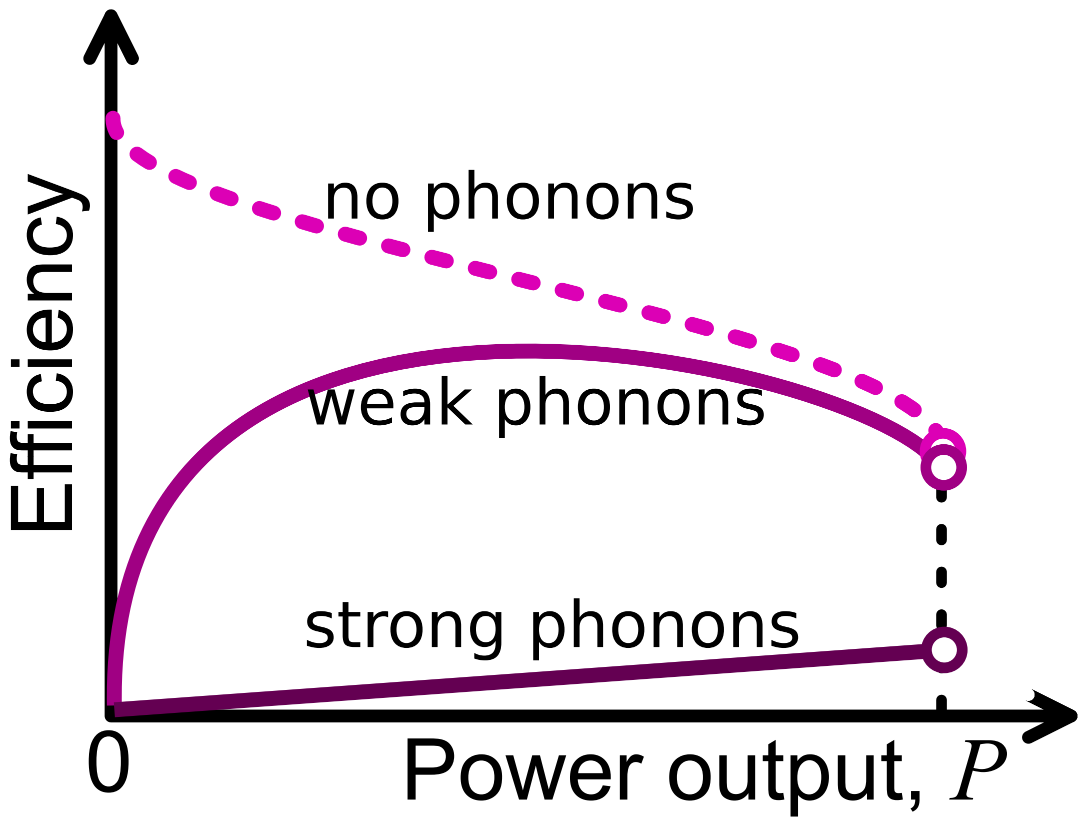


Phenomenological linear-response result, unable to capture the maximum power

Nonlinear result from scattering theory

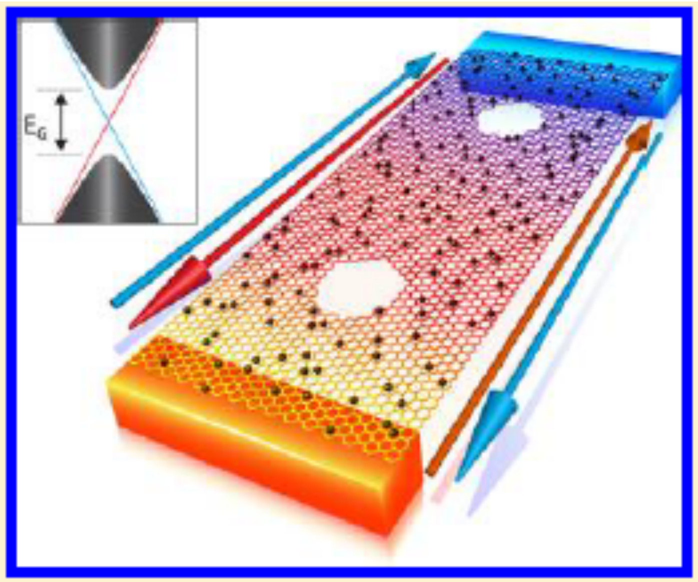
[Whitney, PRL **112**, 130601 (2014)]

Power-efficiency trade-off including phonons

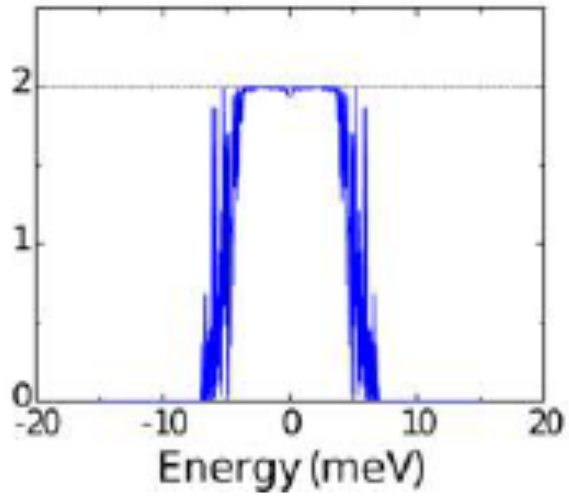


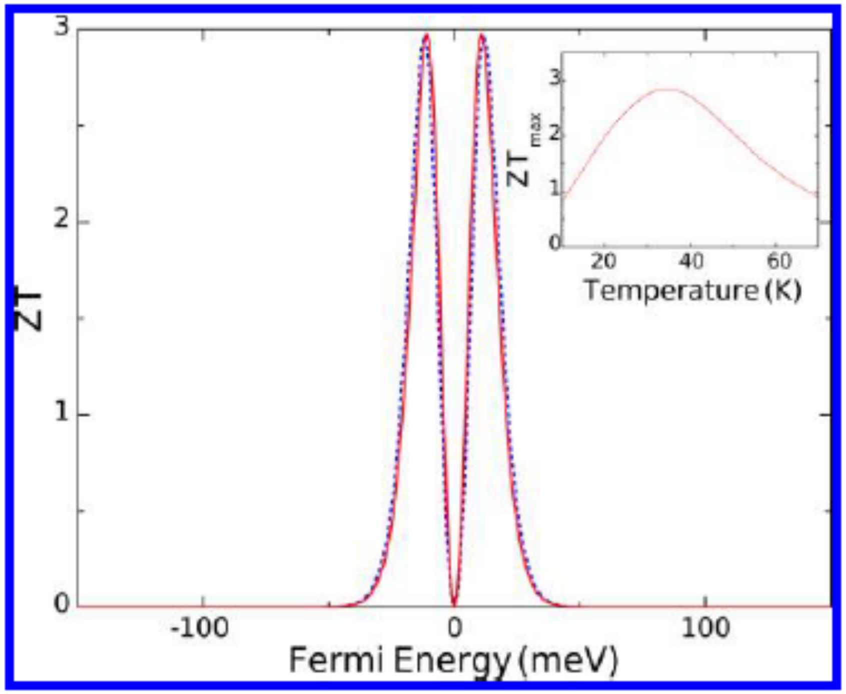
[see Whitney, PRB **91**, 115425 (2015)]

Boxcar transmission in topological insulators



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





Is energy filtering necessary to get Carnot efficiency?

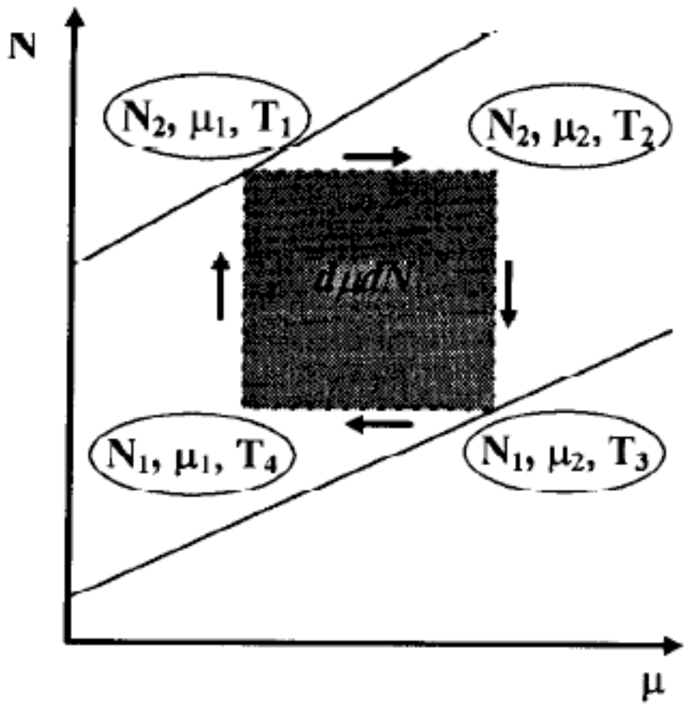
No, for interacting systems with momentum conservation

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

$$1 + ZT = \frac{\kappa'}{\kappa}$$

κ' thermal conductivity at zero electric field

Thermodynamic cycle



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

$$1 + Z_{\mathrm{th}} T = \frac{C_\mu}{C_N}$$

$$C_\mu = \frac{1}{T} \left.\frac{\partial U}{\partial T}\right|_\mu, \quad C_N = \frac{1}{T} \left.\frac{\partial U}{\partial T}\right|_N$$

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

Analogy with a classical gas

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

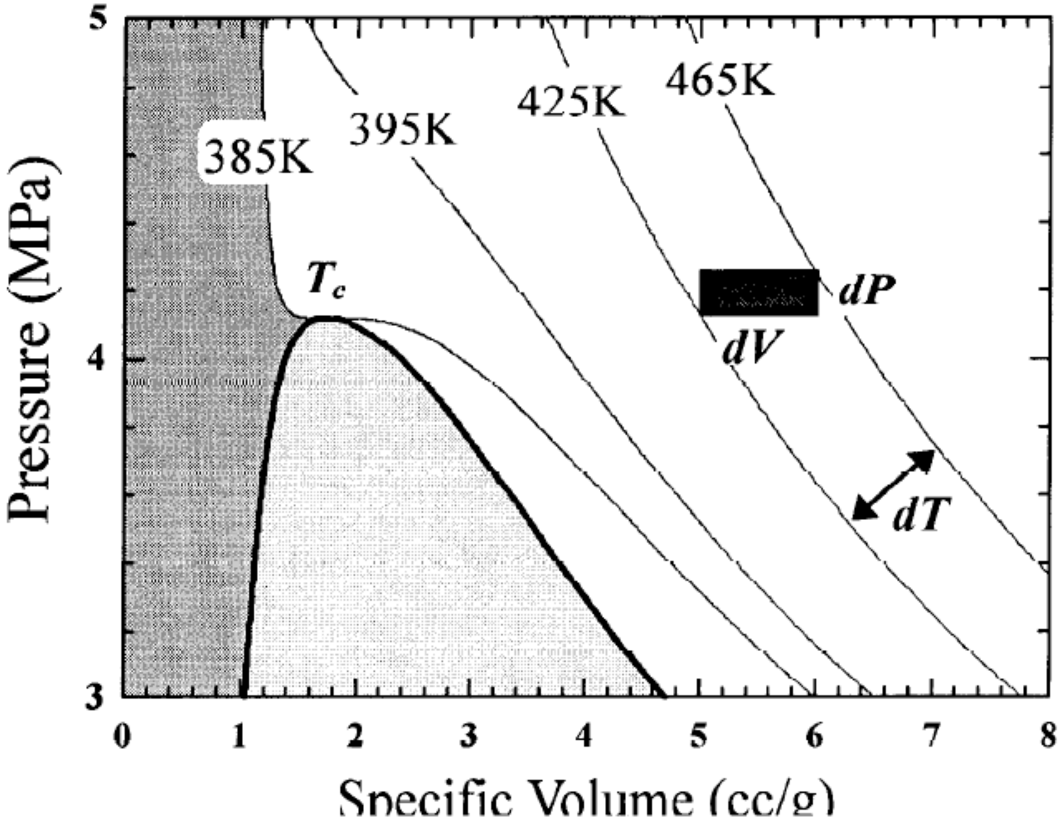


Fig. 5: *PV* diagram for Freon-12 (CCl_2F_2). The two phase region is light gray and the liquid is the darker gray region to the left. Isotherms are indicated by light lines and a typical *dPdV* element is indicated by the rectangle.

$$\frac{\eta}{\eta_C} = \frac{dp\,dV}{d\mathscr{S}\,dT}$$

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

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

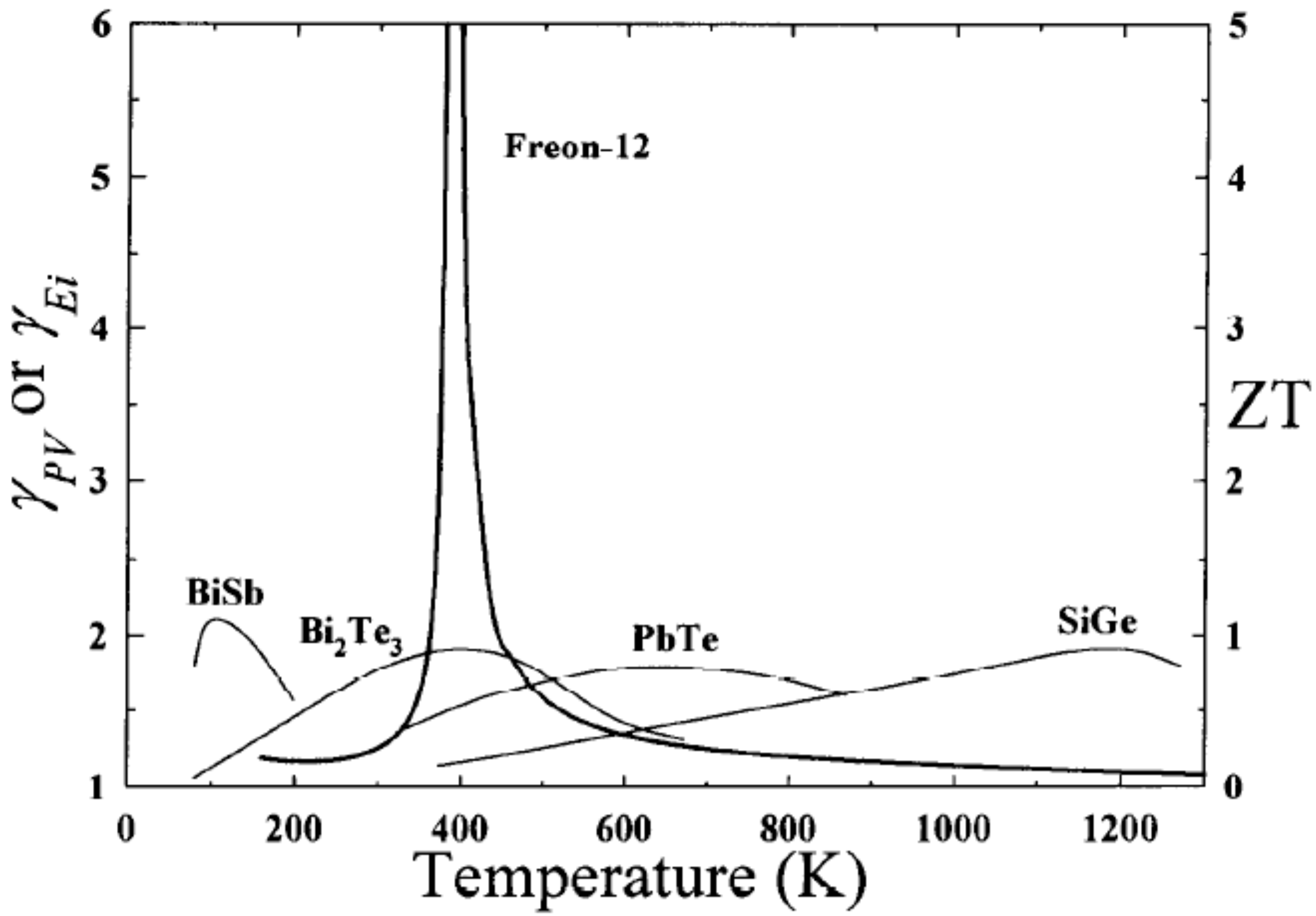
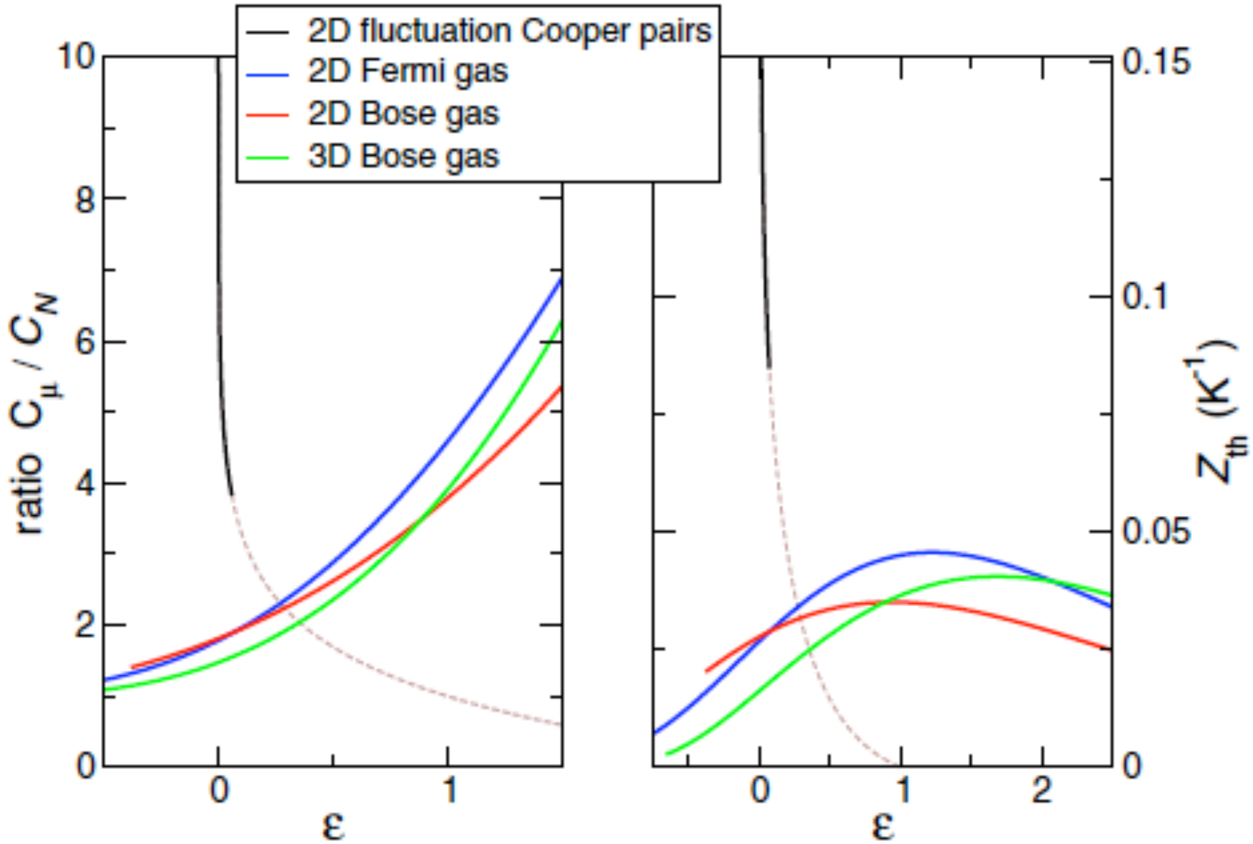


Fig. 4: Specific heat ratios, γ_{PV} for a *PV* system (Freon 12) and thermal conductivity ratios, γ_{Ei}=1+ZT, for selected n-type semiconductor alloys as a function of temperature.

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



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

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

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

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

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

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

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

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 $\det \lambda$ vanishes since

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

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

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

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

$$(\alpha < 1)$$

(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

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

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

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

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 $M = m$ (integrable model)

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

$$J_\rho = \gamma_L - \gamma_R.$$

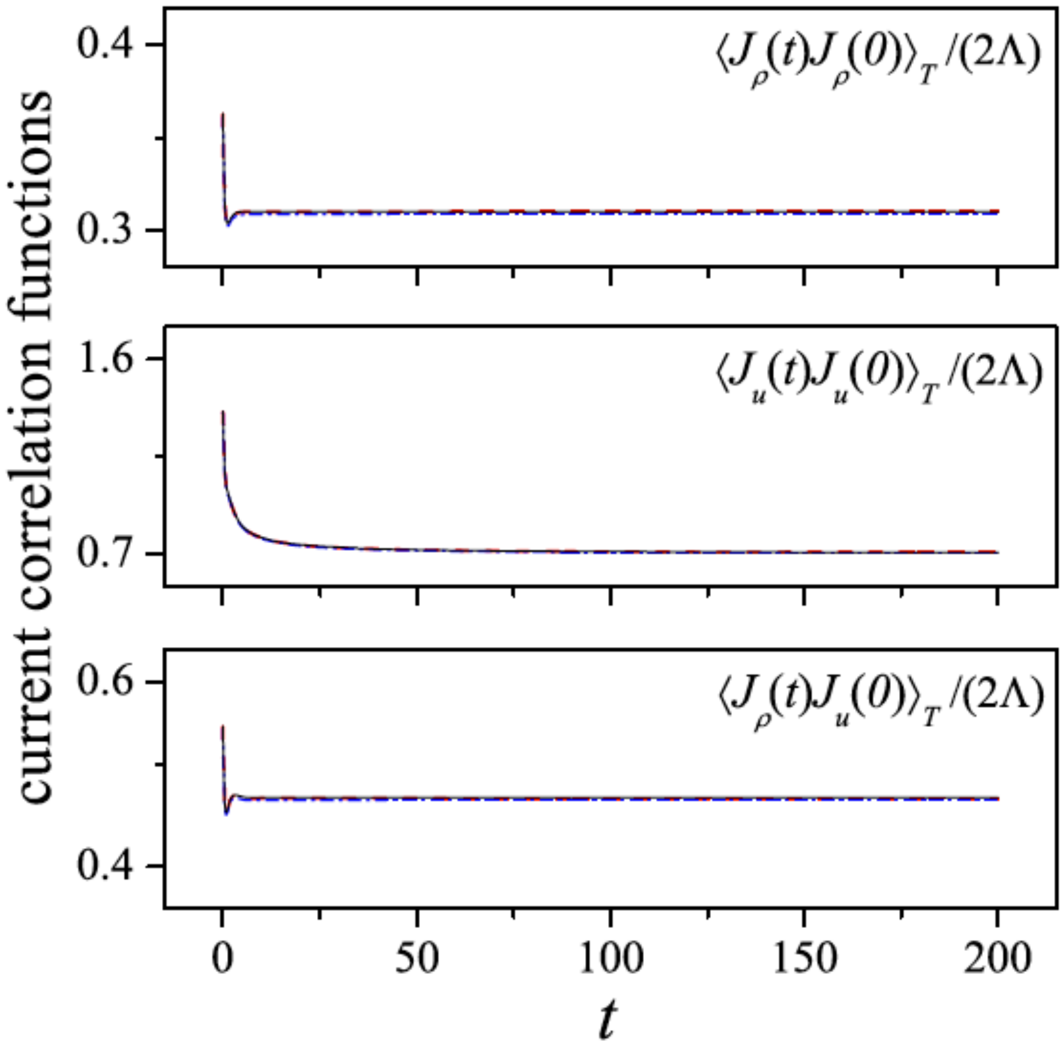
$ZT = 1$ (at $\mu = 0$)

$$\gamma_\alpha = \frac{1}{h\beta_\alpha} e^{\beta_\alpha \mu_\alpha}$$

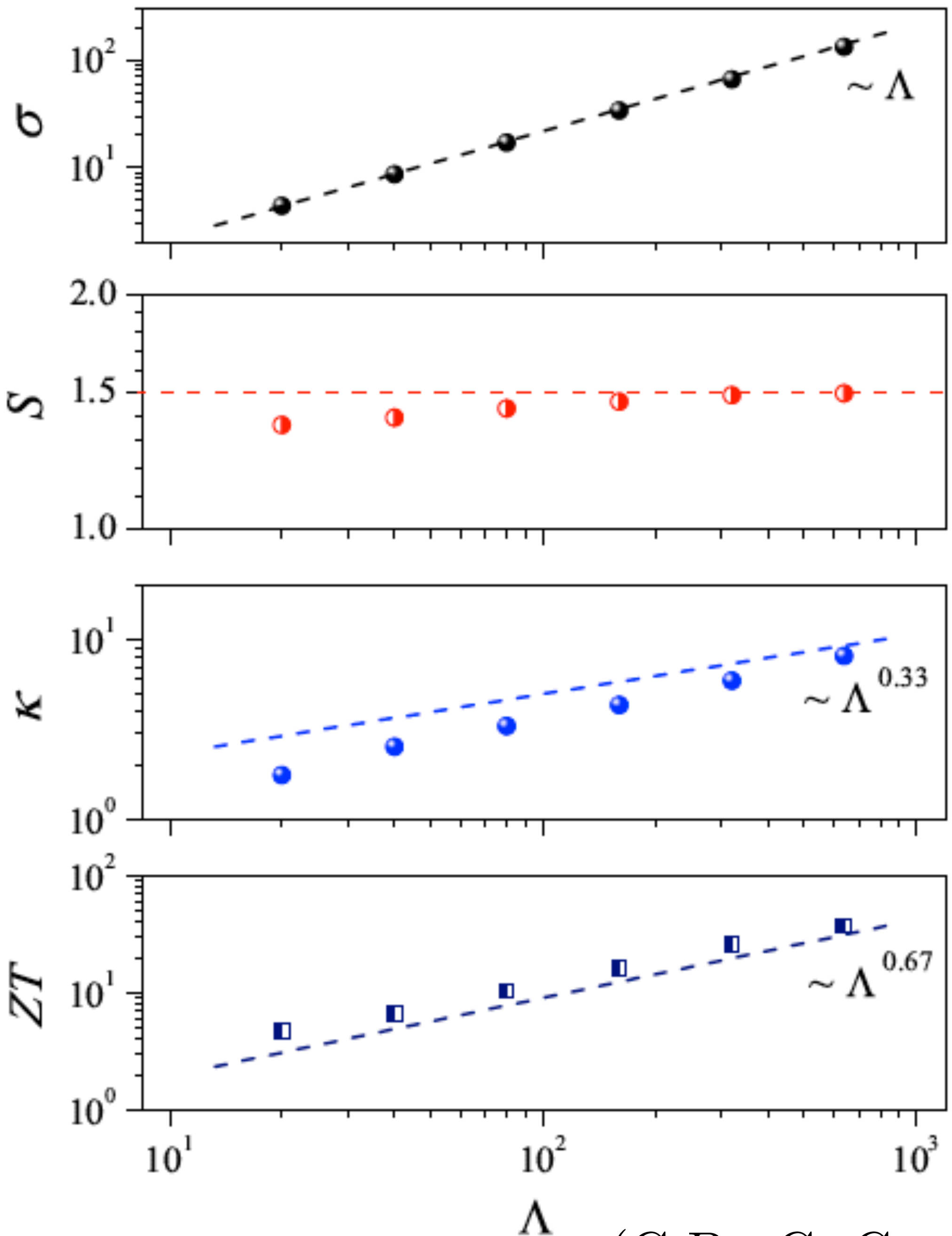
injection rates

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

Non-decaying correlation functions



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



Anomalous thermal transport

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

ZT diverges increasing the systems size

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

Energy-filtering mechanism?

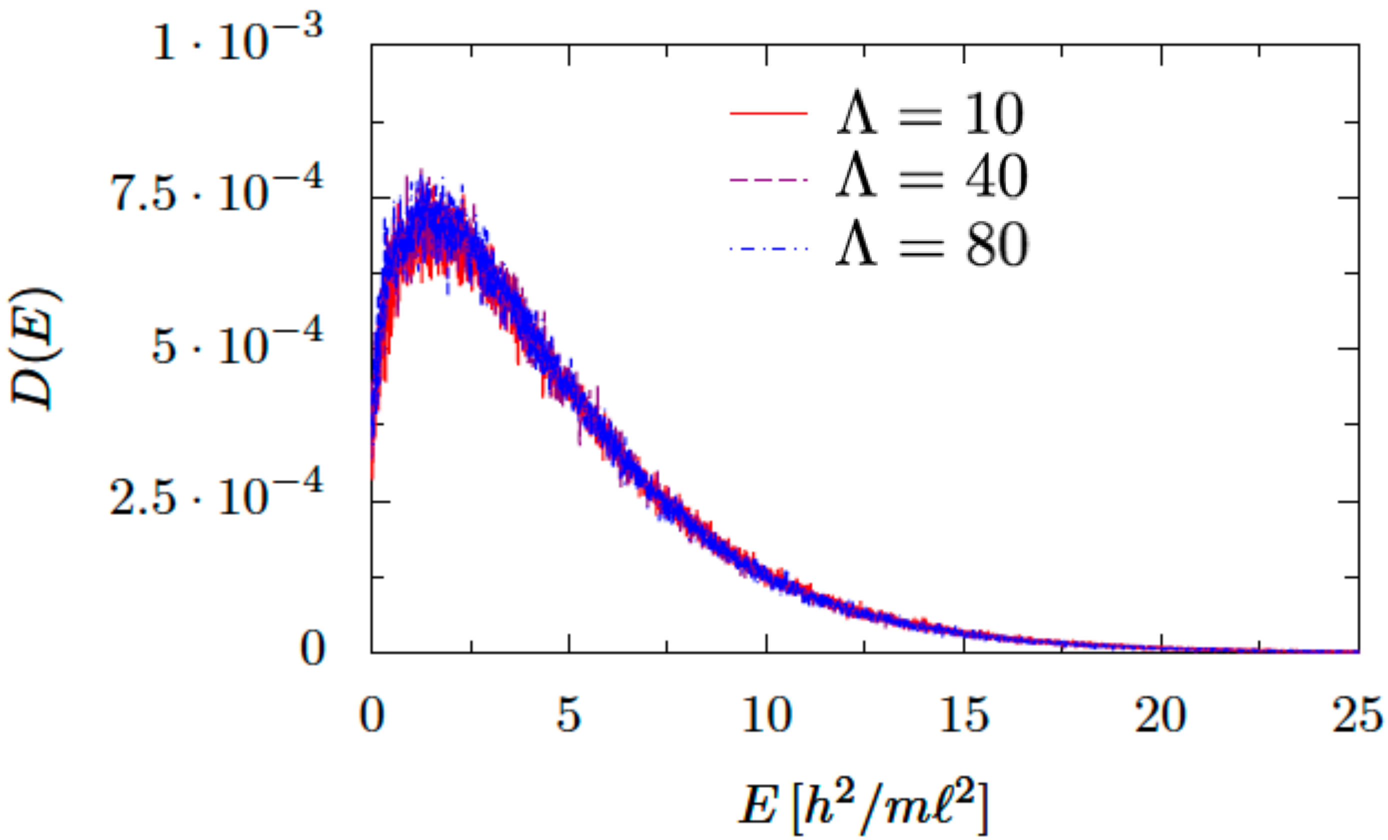
At a given position x compute:

$$J_\rho = \int_0^\infty dE\, D(E)$$

$D(E) \equiv D_L(E) - D_R(E)$ **"transmission function"**

$D_L(E)$ **Density of particles crossing x from left**

$D_R(E)$ **Density of particles crossing x from right**



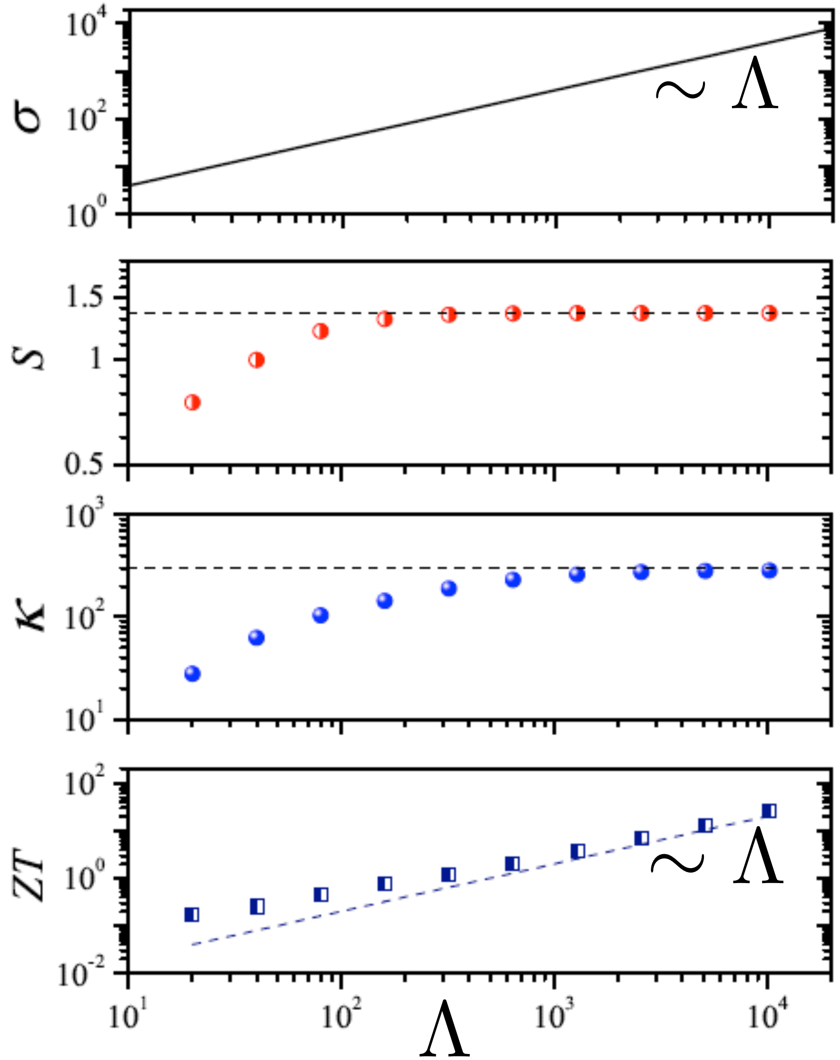
There is no sign of narrowing of D(E) with increasing the system size L

A mechanism for increasing ZT different from energy filtering is needed

(K. Saito, G.B., G. Casati, Chem. Phys. 375, 508 (2010))

1D (screened) Coulomb gas model

$$H = \sum_i \left[\frac{p_i^2}{2m_i} + U(x_i - x_{i-1}) \right], \qquad U(x) = a/x$$



Fourier-like behavior

(S. Chen, J. Wang , G. Casati, G.B., PRE 92, 032139 (2015))

Multiparticle collision dynamics (Kapral model)

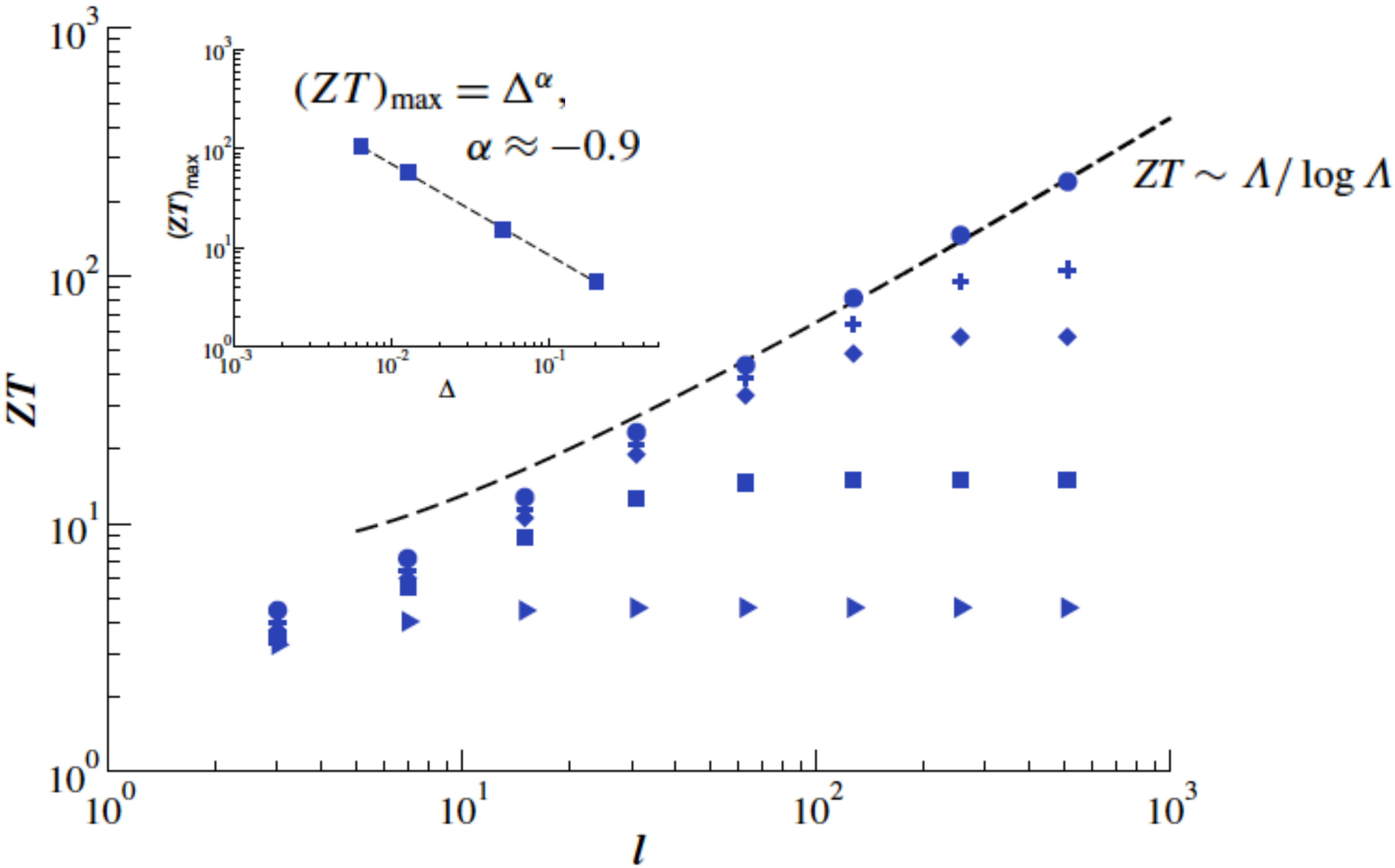
Streaming step: free propagation during a time τ

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

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

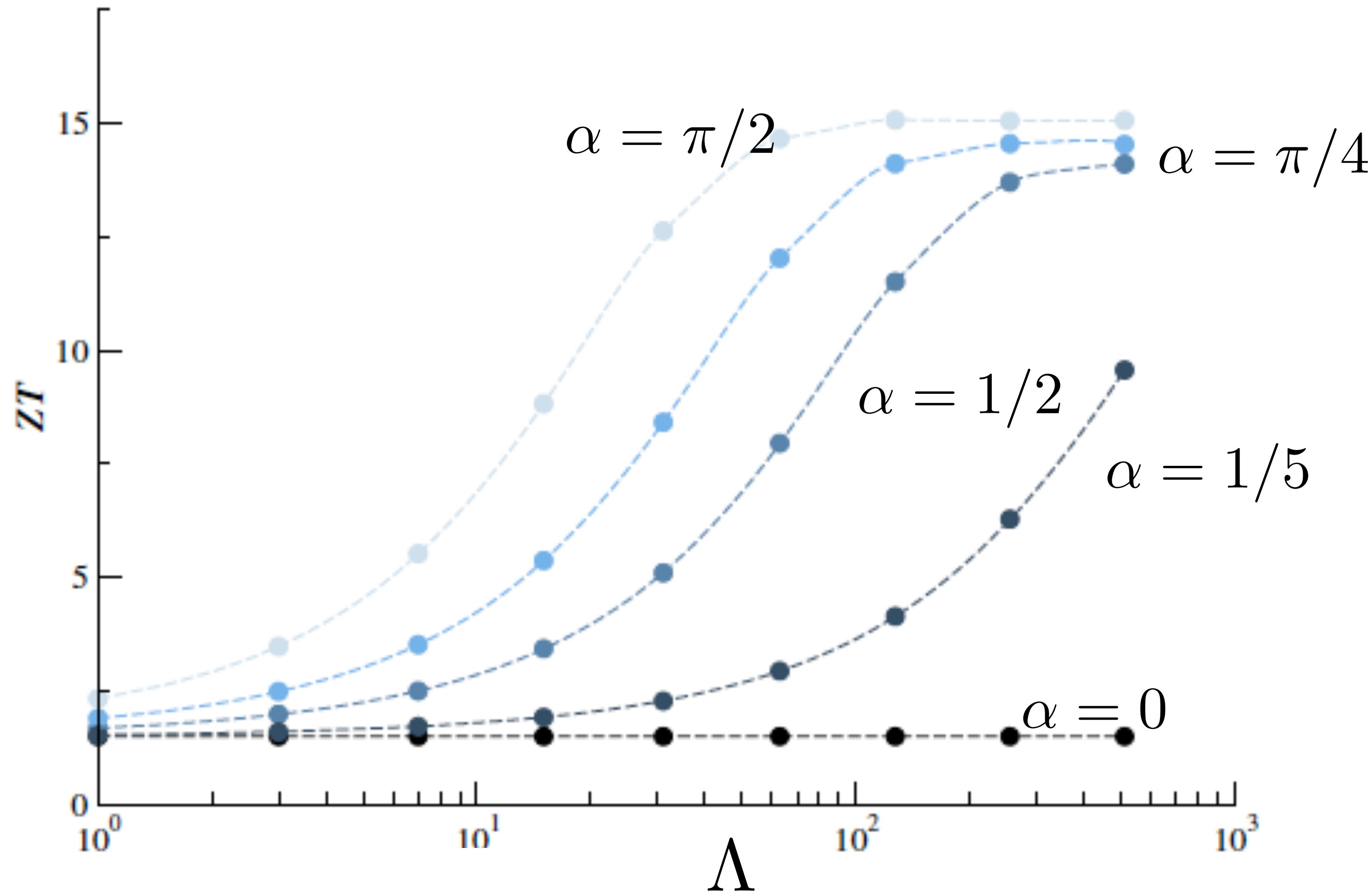
$$\vec{v}_i \longrightarrow \vec{V}_{\mathrm{CM}} + \hat{\mathcal{R}}^{\pm\alpha}\left(\vec{v}_i - \vec{V}_{\mathrm{CM}}\right)$$

Momentum is conserved



The range of linear response shrinks with the system size: Carnot efficiency achieved at zero power

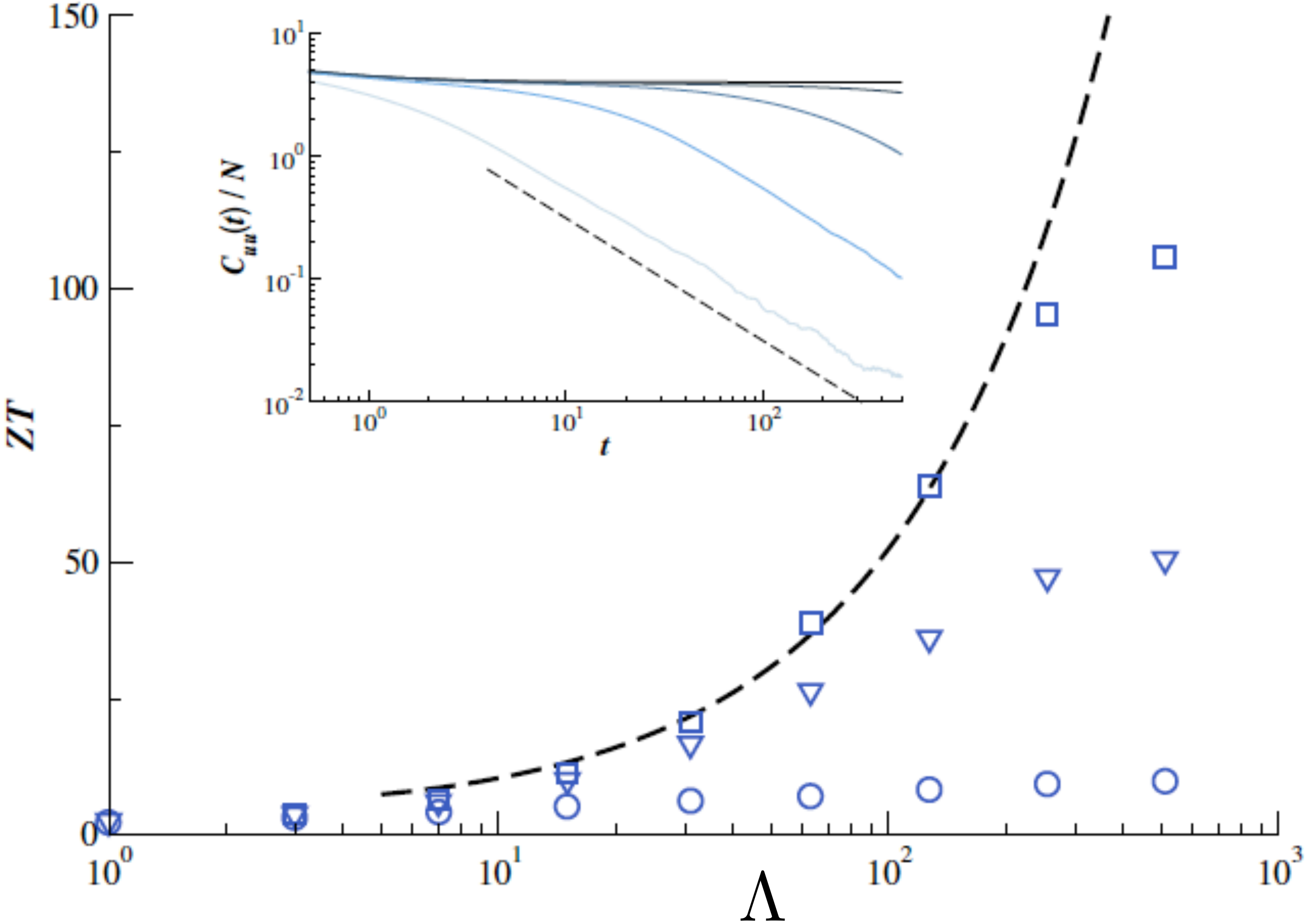
2D simulations (Kapral model)



A free gas of charged interacting particles (electrons,..) has diverging ZT at the thermodynamic limit

(G.B., G. Casati, C. Mejía-Monasterio, New J. Phys. 16, 015014 (2014))

Breaking of momentum conservation



Noise mimicking disorder effects breaking momentum conservations; correlations decay and ZT saturates

Summary for momentum-conserving systems

New mechanism for achieving Carnot efficiency in extended interacting systems, provided:

1) Overall momentum is the only relevant constant of motion (translational invariance of interactions, absence of on-site pinning potential)

2) Absence of dissipative channels

Mechanism fundamentally different from energy filtering

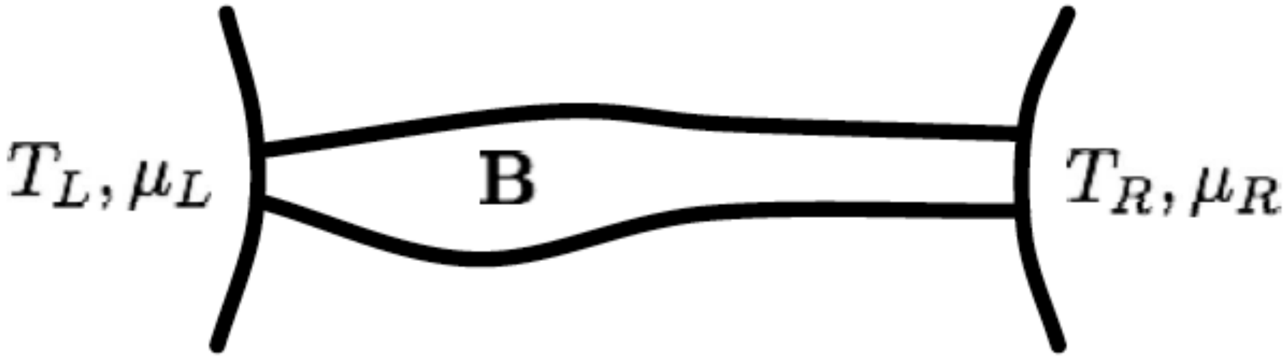
No dimensionality restrictions, argument in principle applicable also to quantum systems

Possible implementations in high-mobility 2D electron gases? (elastic mean free paths up to tens of microns)

Is the tight coupling condition necessary to get Carnot efficiency?

No, for systems without time-reversal symmetry

Linear response 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 $T_L > T_R, \quad \mu_L < \mu_R$)

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:

$$L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B}) \quad \Rightarrow \quad \begin{aligned} &G(\mathbf{B}) = G(-\mathbf{B}) \\ &K(\mathbf{B}) = K(-\mathbf{B}) \\ &\text{in general, } S(\mathbf{B}) \neq S(-\mathbf{B}) \end{aligned}$$

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

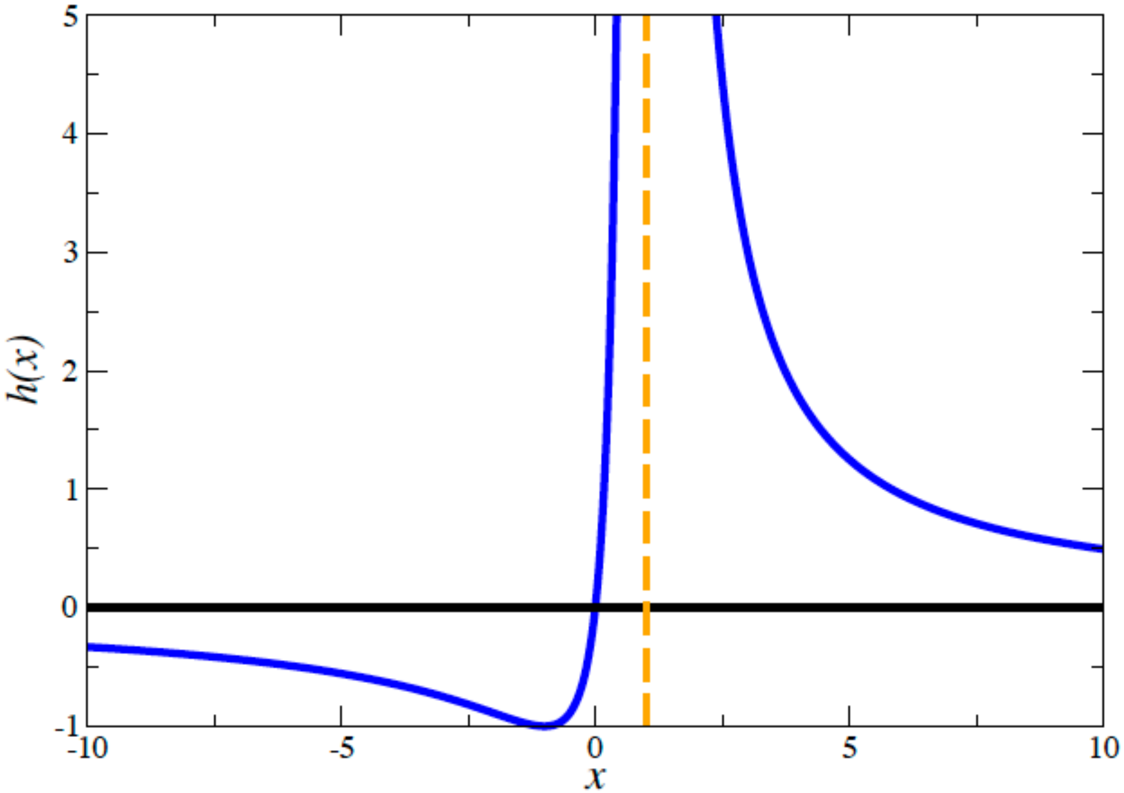
$$x = \frac{L_{eh}}{L_{he}} = \frac{S(\boldsymbol{B})}{S(-\boldsymbol{B})}$$

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

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

At $B=0$ there is time-reversibility and:
asymmetry parameter $x=1$
the efficiency only depends on $y(x=1)=ZT$

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

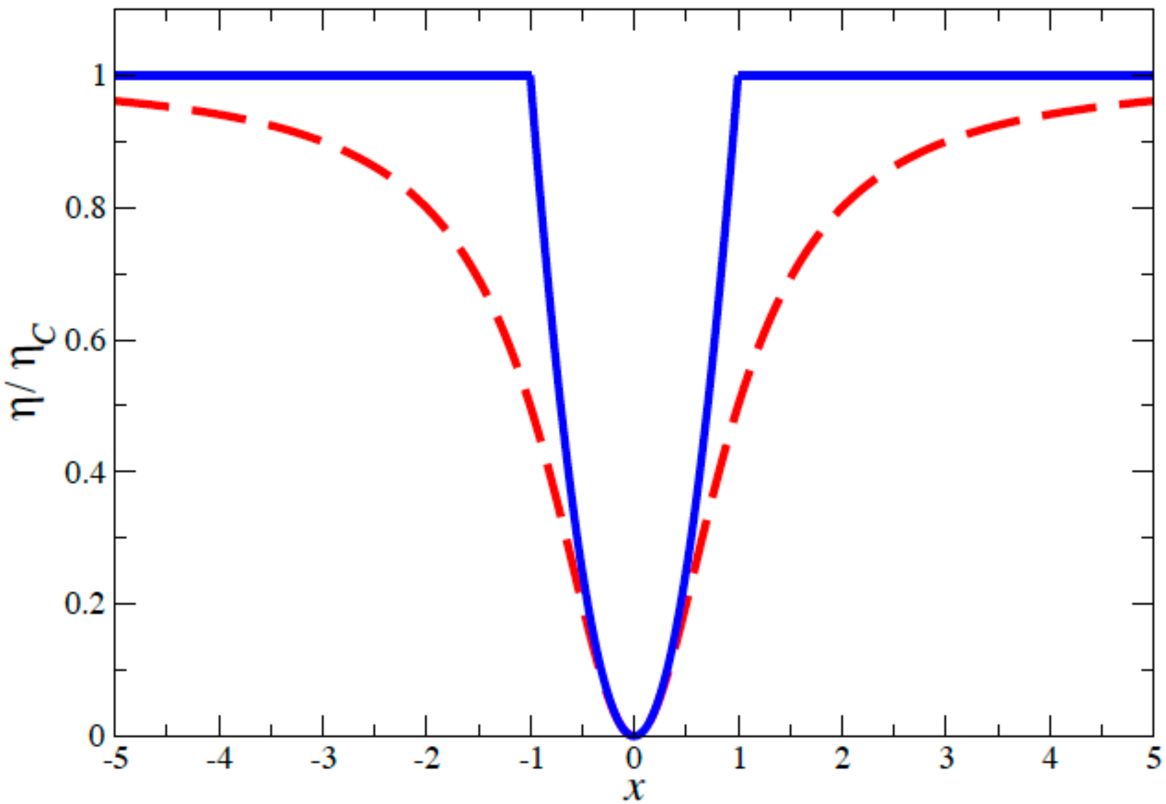


$$h(x) = 4x/(x-1)^2$$

maximum efficiencies

achieved for $y = h(x)$

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



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

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

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

Output power at maximum efficiency

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

When time-reversibility is broken, <u>within linear response</u> it is in principle 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.

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 do 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?

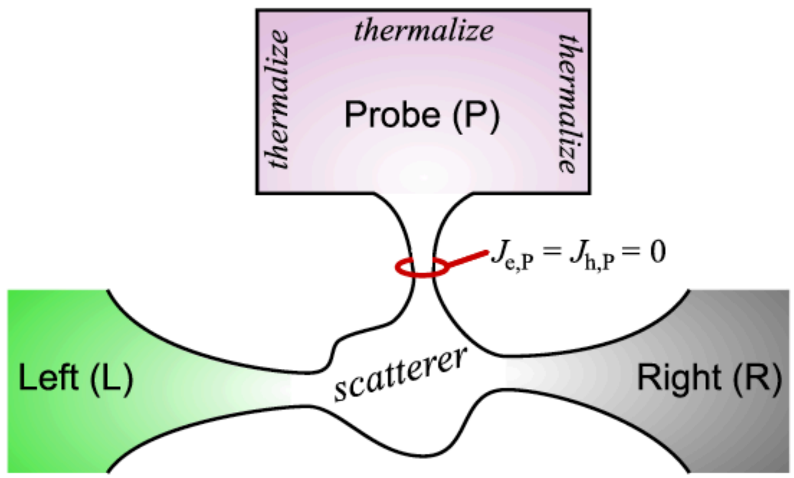
For non-interacting systems, due to the symmetry properties of the scattering matrix ⇨ $S(\mathbf{B}) = S(-\mathbf{B})$

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

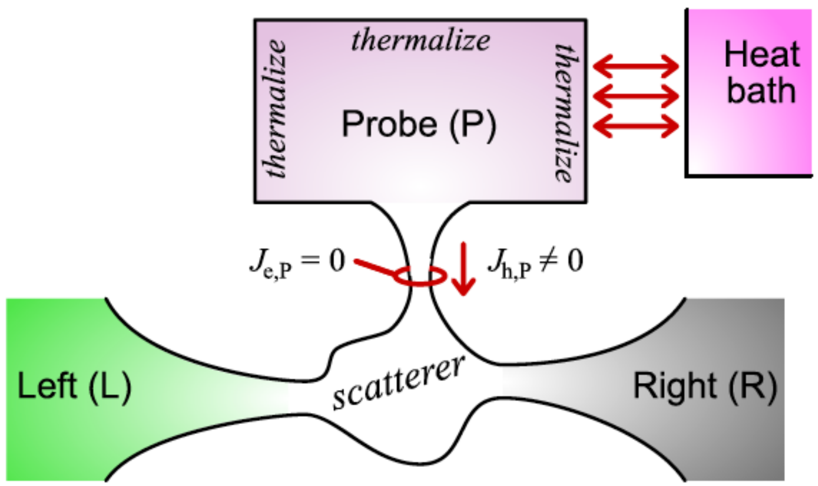
Let us consider the case of partially coherent transport, with inelastic processes simulated by **"conceptual probes"** (Buttiker, 1988).

Physical model of probe reservoirs

Large but finite “reservoirs”

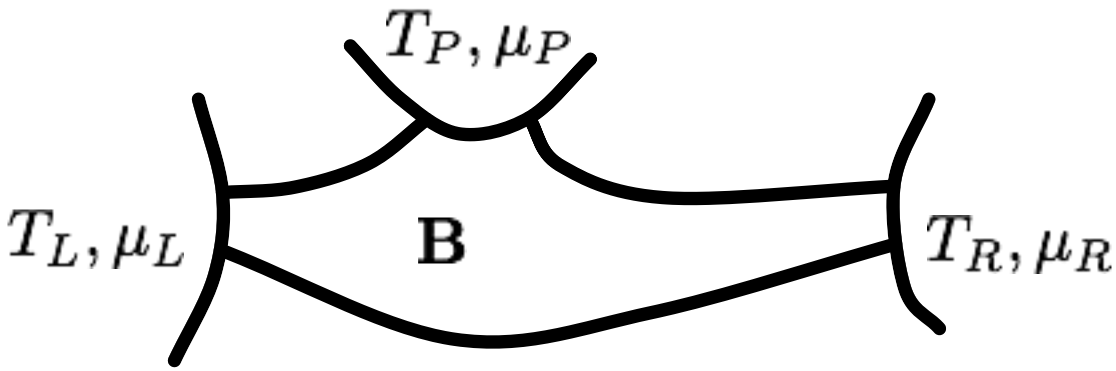


Voltage and temperature probe



Voltage probe

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

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

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

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

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

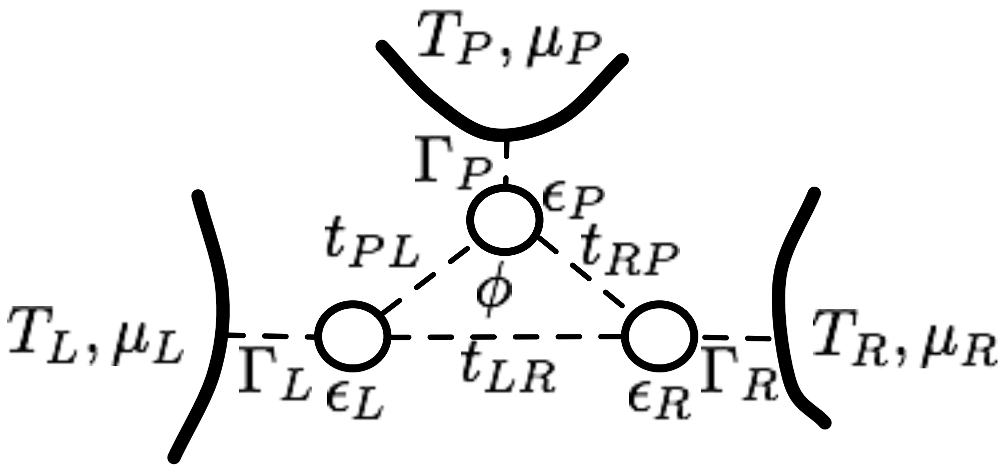
Broadening functions $\Gamma_k(E) \equiv i[\Sigma_k(E) - \Sigma_k^\dagger(E)]$

Self-energies Σ_k

Retarded system's Green function

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

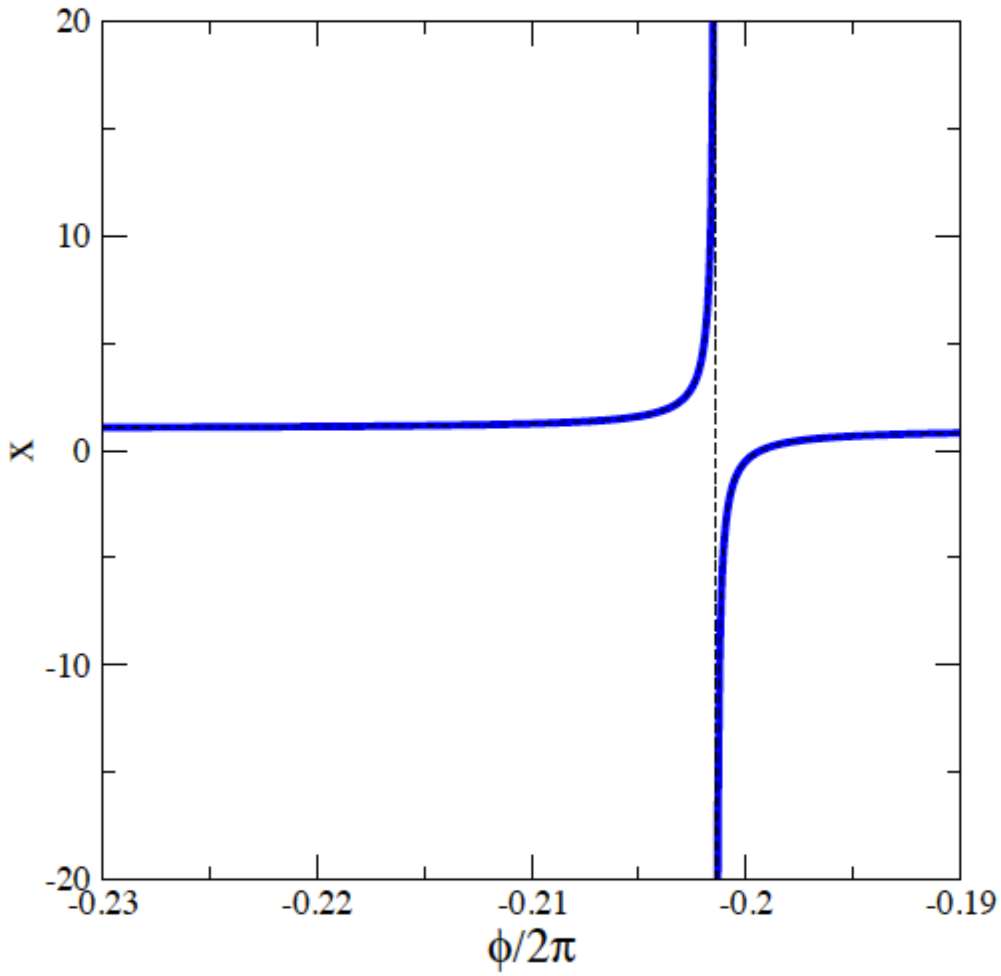
Illustrative three-dot example



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

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

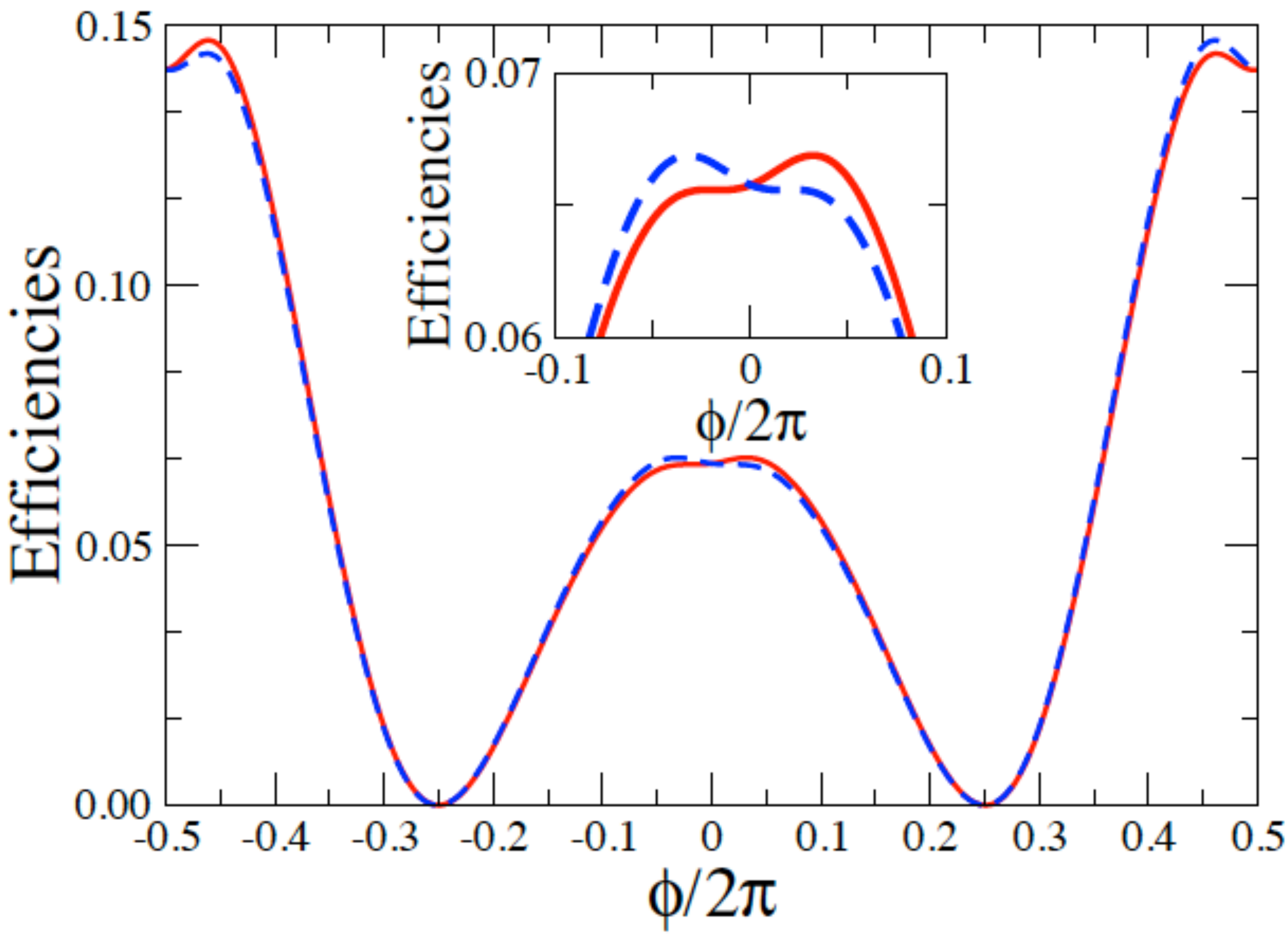
When a magnetic field is added, the efficiencies of power generation and refrigeration are no longer equal:

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

To linear order in the applied magnetic field:

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

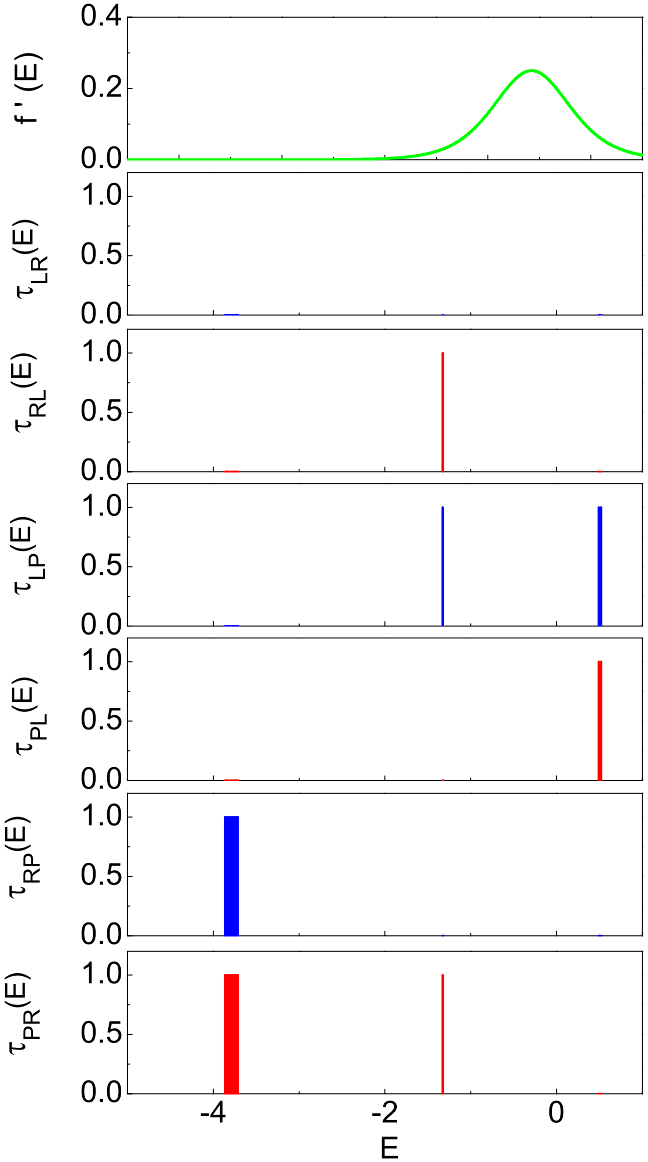
A small magnetic field improves either power generation or refrigeration, and vice versa if we reverse the direction of the field



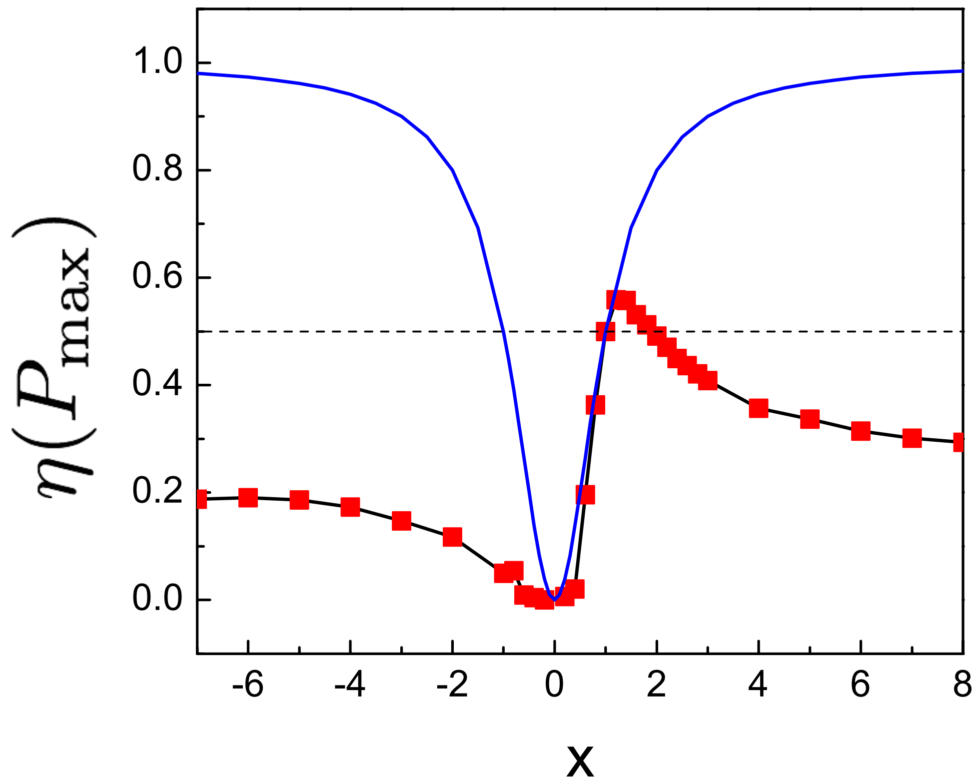
The large-field enhancement of efficiencies is model-dependent, but the small-field asymmetry is generic

Transmission windows model

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



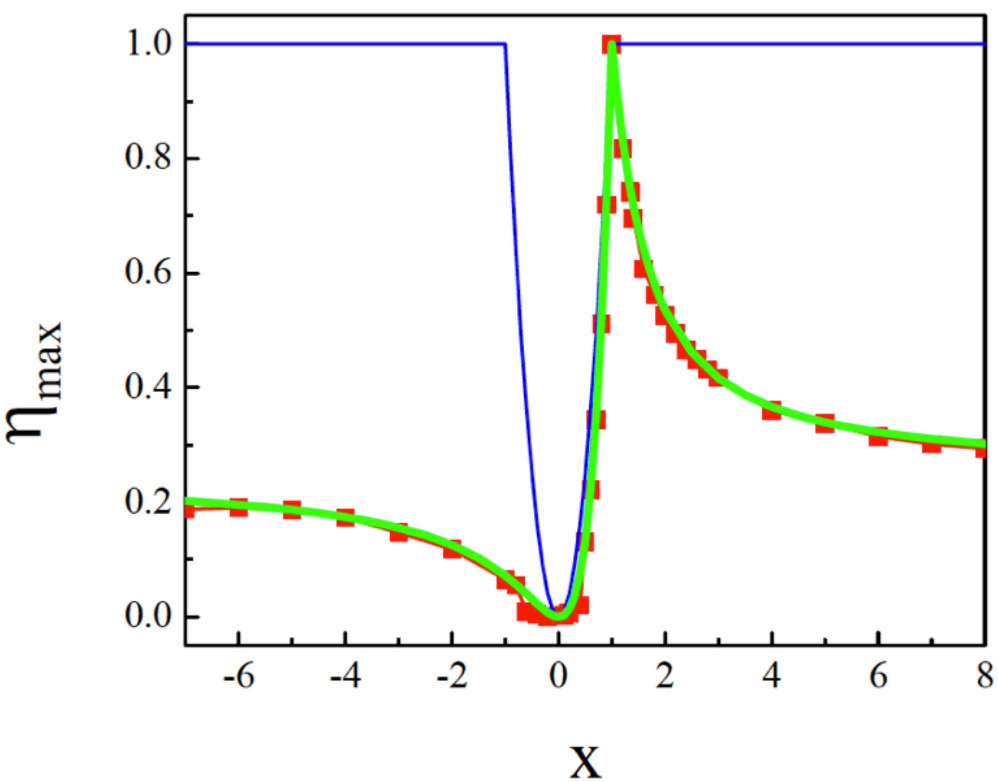
The Curzon-Ahlborn limit can be overcome (within linear response)

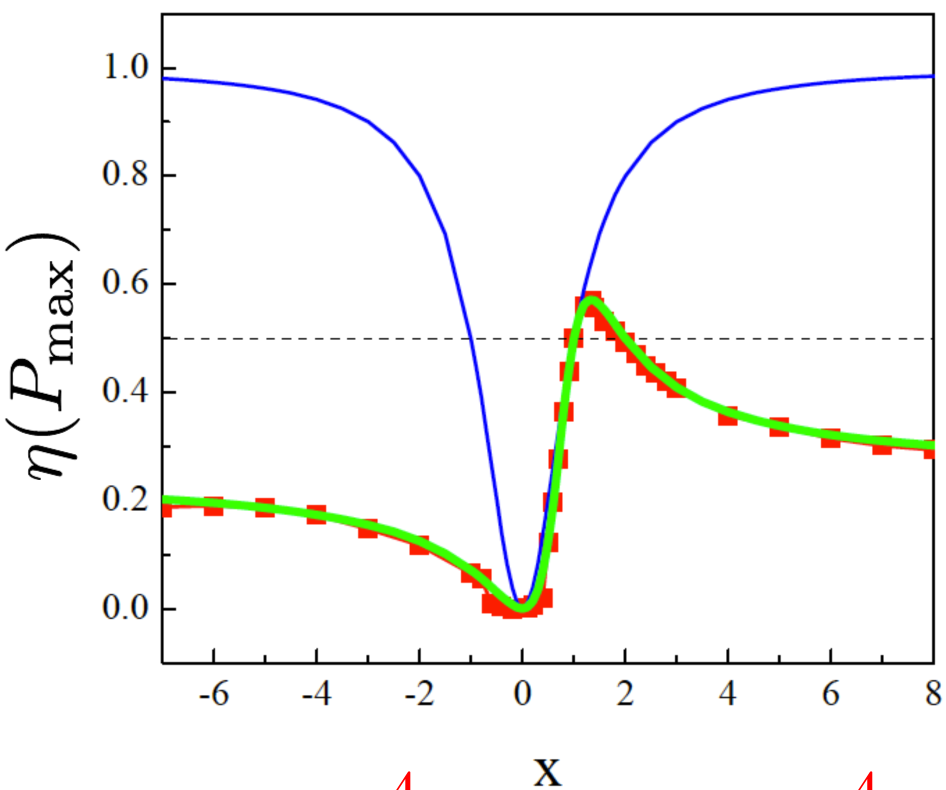


(V. Balachandran, G. B., G. Casati, PRB **87**, 165419 (2013));
se also M. Horvat, T. Prosen, G. B., G. Casati, PRE **86**, 052102 (2012))

Saturation of bounds from the unitarity of S-matrix

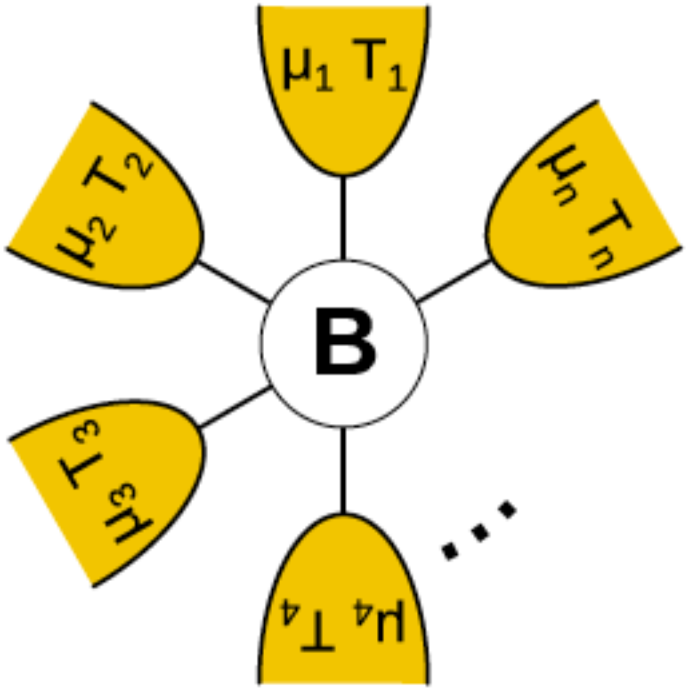
Bounds obtained for non-interacting 3-terminal transport
(K. Brandner, K. Saito, U. Seifert, PRL **110**, 070603 (2013))

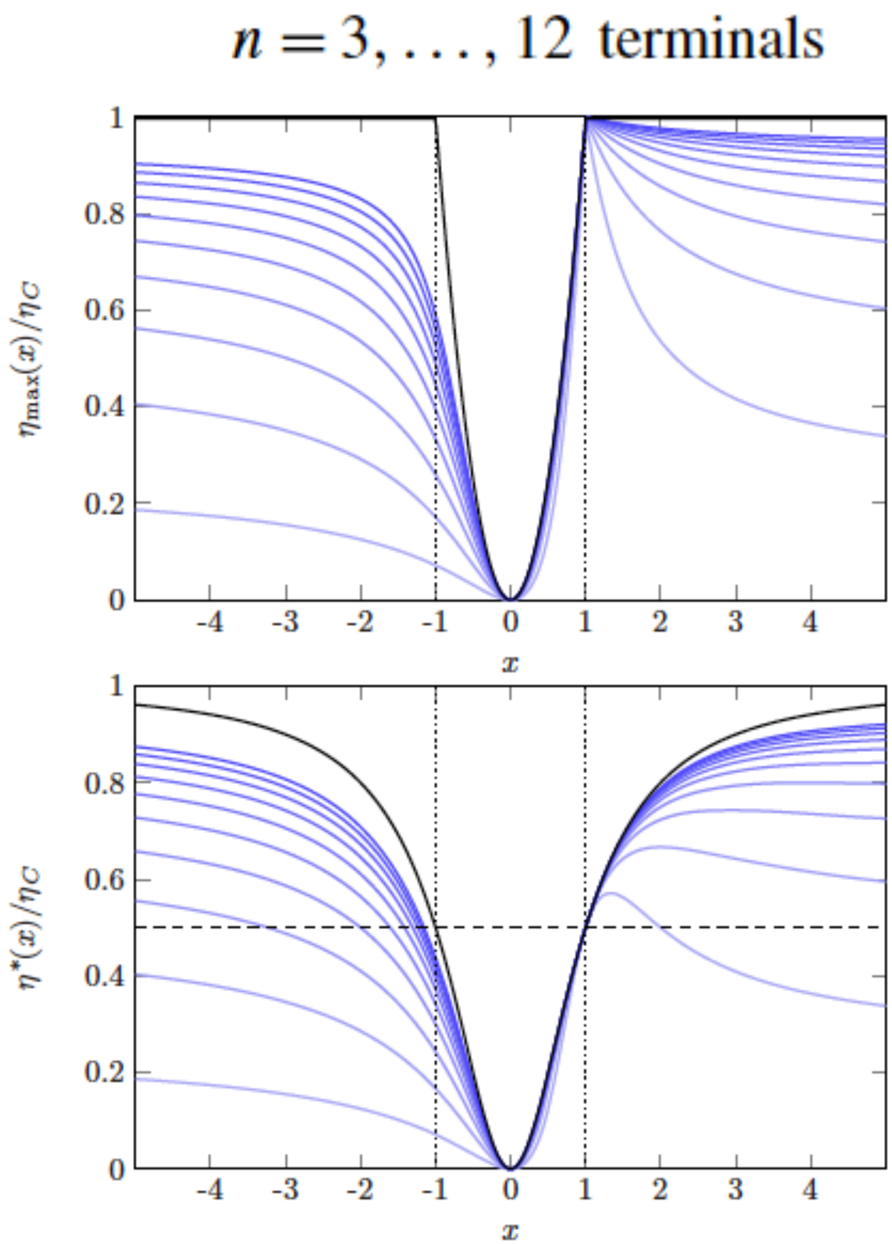




$$\eta(P_{max}) = \frac{4}{7}\eta_C \quad \text{at} \quad x = \frac{4}{3}$$

Bounds for multi-terminal thermoelectricity

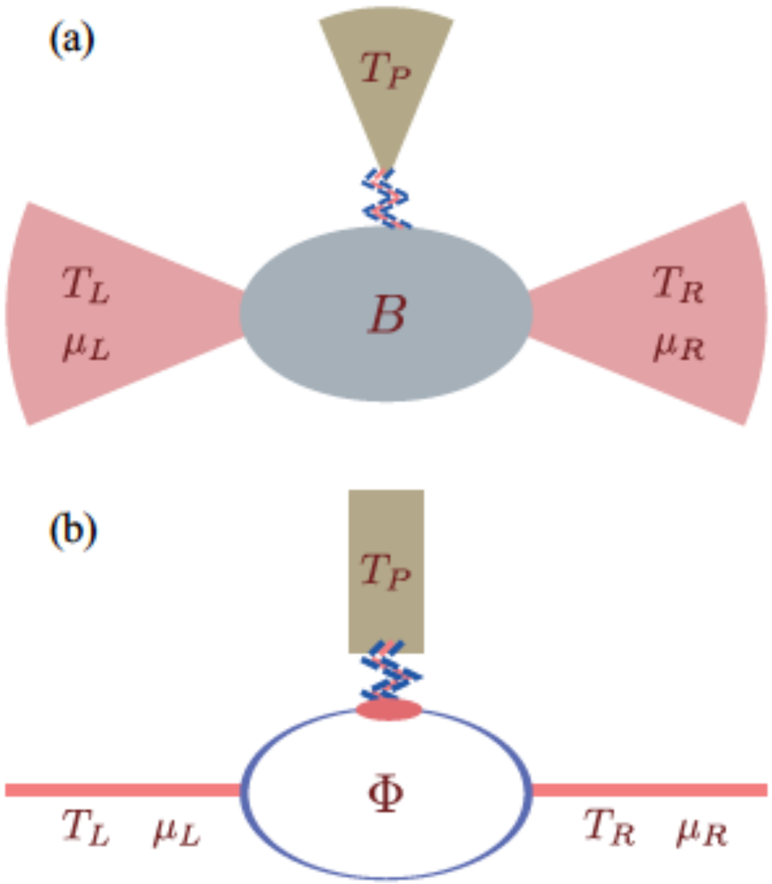


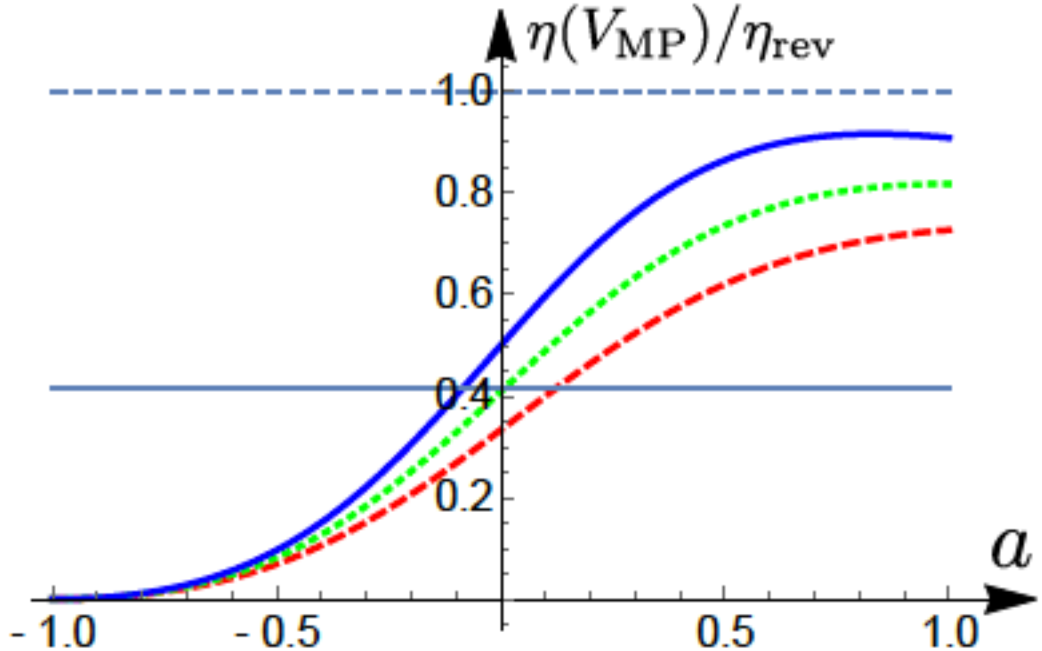


Numerical evidence that the power vanishes when the Carnot efficiency is approached

(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))

Summary for systems with magnetic field

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

Carnot efficiency in principle achievable far from the tight coupling regime and with finite power (within linear response)

The CA limit can be overcome within linear response

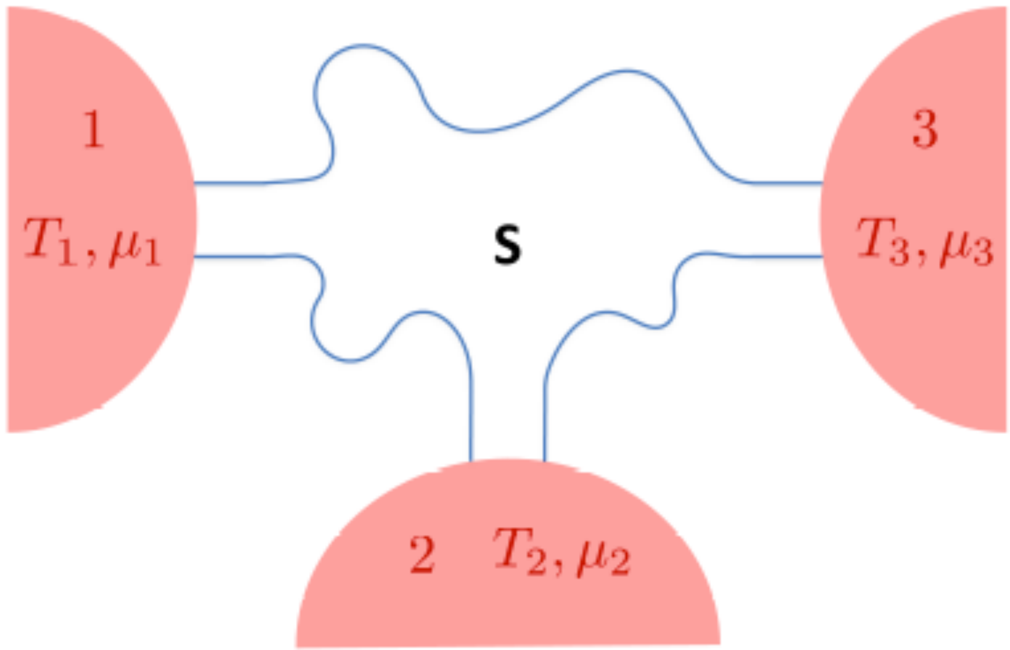
For partially coherent transport in asymmetric structures the Seebeck coefficient is not an even function of the field

Asymmetric efficiencies for 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?

Multi-terminal thermoelectricity

Possibility to exploit additional terminals to decouple charge and heat flows and improve thermoelectric efficiency?



The third terminal is not necessarily a probe

Multi-terminal transport coefficients

Nonlocal thermopowers

$$S_{ij} = -\left(\frac{\Delta V_i}{\Delta T_j}\right)_{\substack{J_{e,k}=0,\ \forall k,\\ \Delta T_k=0,\ \forall k\neq j}}$$

Electrical and thermal conductances

$$G_{ij} = \left(\frac{J_{e,i}}{\Delta V_j}\right)_{\substack{\Delta T_k=0,\ \forall k,\\ \Delta V_k=0,\ \forall k\neq j}} \qquad K_{ij} = \left(\frac{J_{h,i}}{\Delta T_j}\right)_{\substack{J_{e,k}=0,\ \forall k,\\ \Delta T_k=0,\ \forall k\neq j}}$$

Peltier coefficients

$$\Pi_{ij} = \left(\frac{J_{h,i}}{J_{e,j}}\right)_{\substack{\Delta T_k=0,\ \forall k,\\ \Delta V_k=0,\ \forall k\neq j}} \qquad \Pi_{ij}(\boldsymbol{B}) = T S_{ji}(-\boldsymbol{B})$$

(F. Mazza, R. Bosisio, G. B., V. Giovannetti, R. Fazio, F. Taddei, New J. Phys. **16**, 085001 (2014))

Thermoelectric efficiency

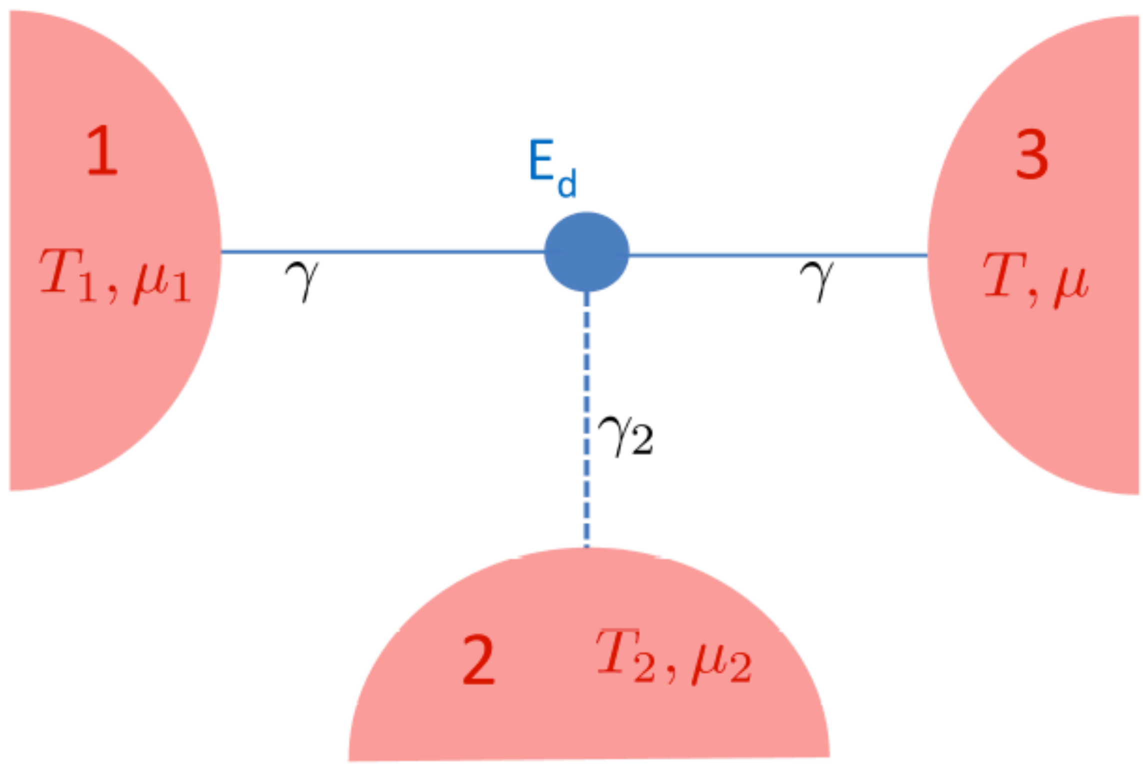
$$\eta = \frac{\dot{W}}{\sum_{k_+} J_{h,k}} = \frac{\sum_{k=1}^{n} J_{h,k}}{\sum_{k_+} J_{h,k}} = \frac{-\sum_{k=1}^{n}(\mu_k/e)J_{e,k}}{\sum_{k_+} J_{h,k}}$$

The sum in the denominator is restricted to positive heat currents only

Various instances are possible and for all of them, in the three-terminal case, explicit formulas for the efficiency at maximum power have been worked out

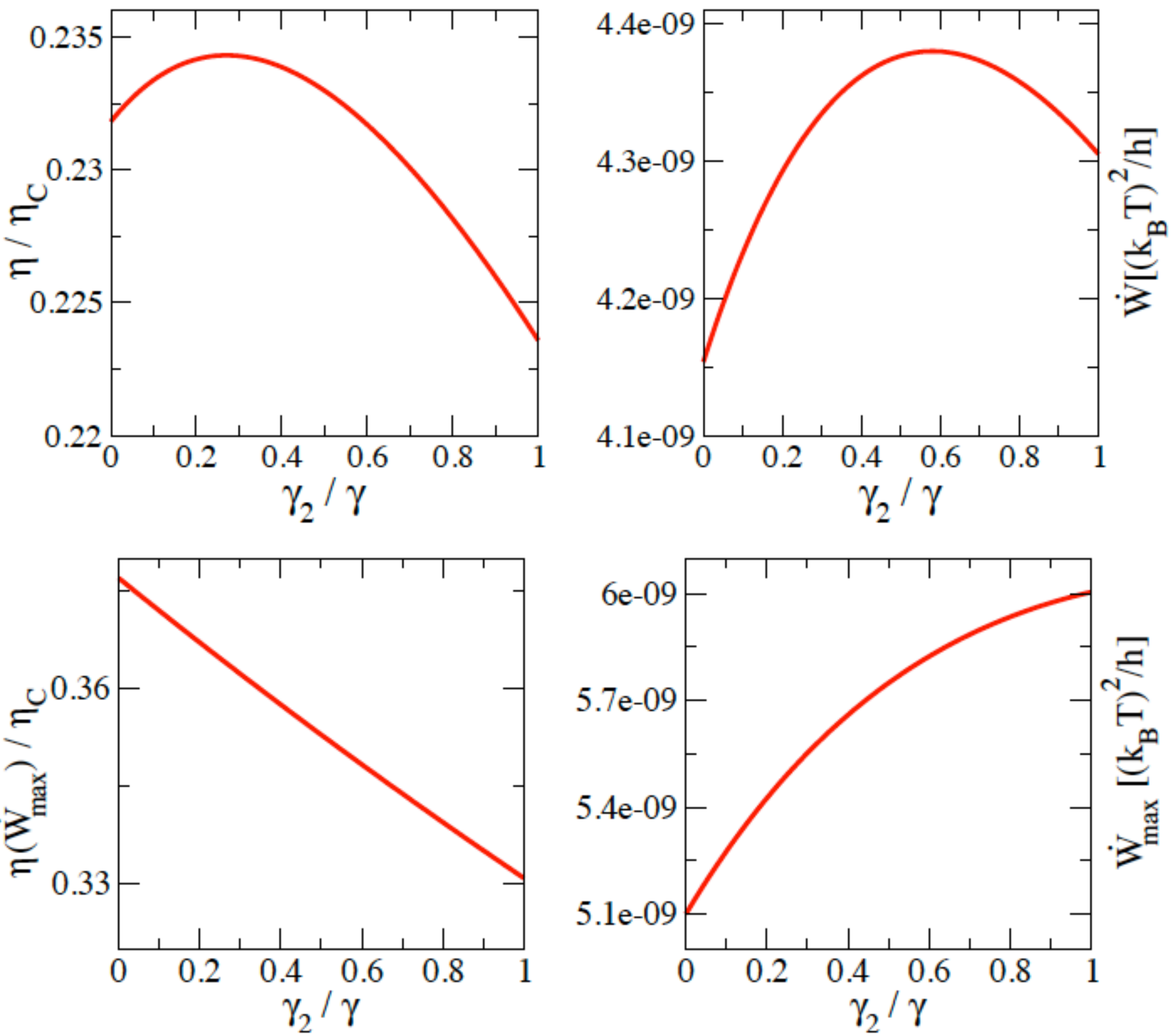
(F. Mazza, R. Bosisio, G. B., V. Giovannetti, R. Fazio, F. Taddei, New J. Phys. **16**, 085001 (2014))

Illustrative example: single dot

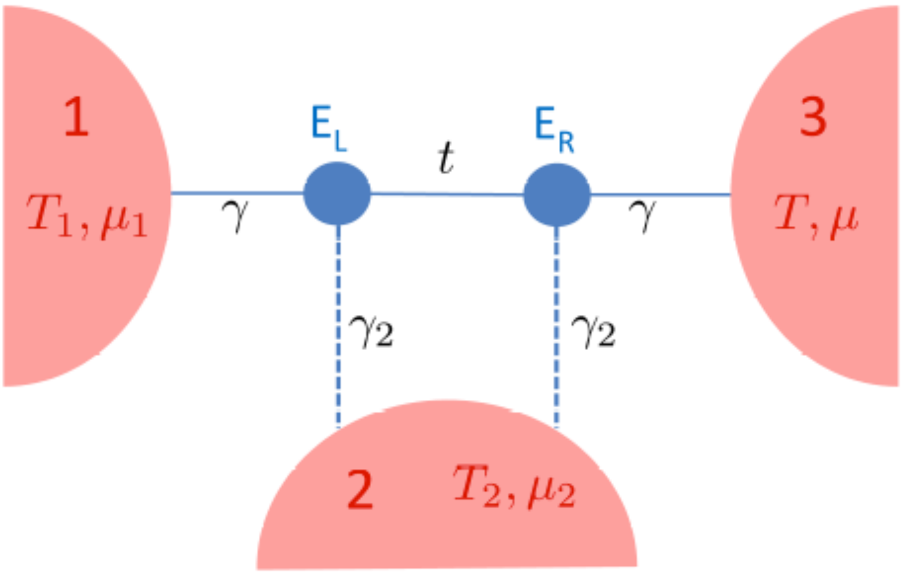


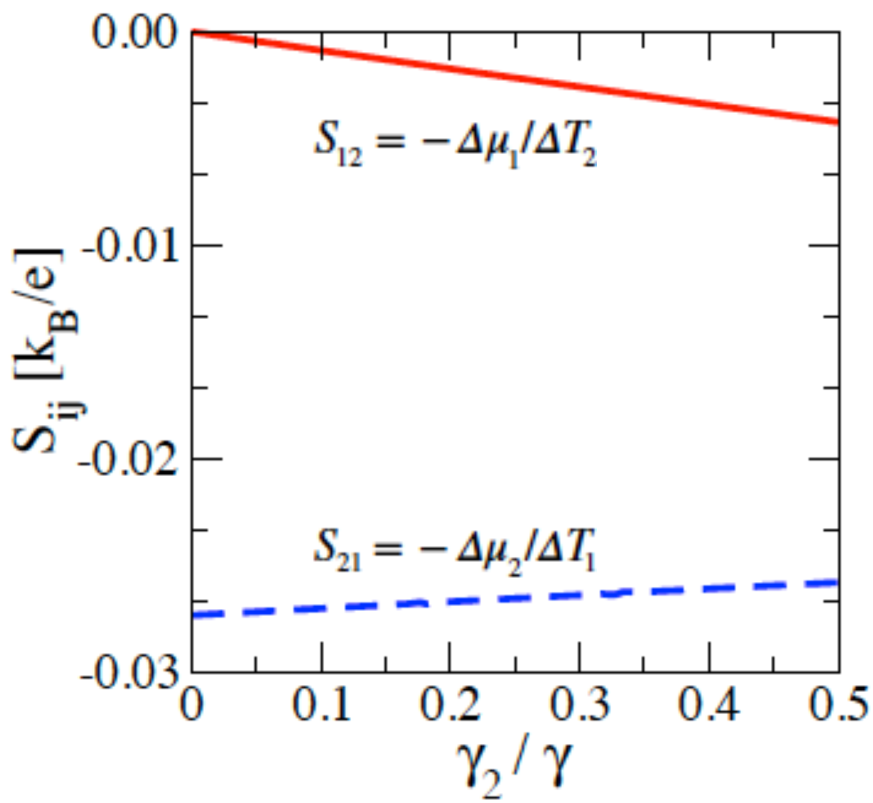
Terminal 2 is at temperature between T_1 and T_3

Improving power and/or efficiency



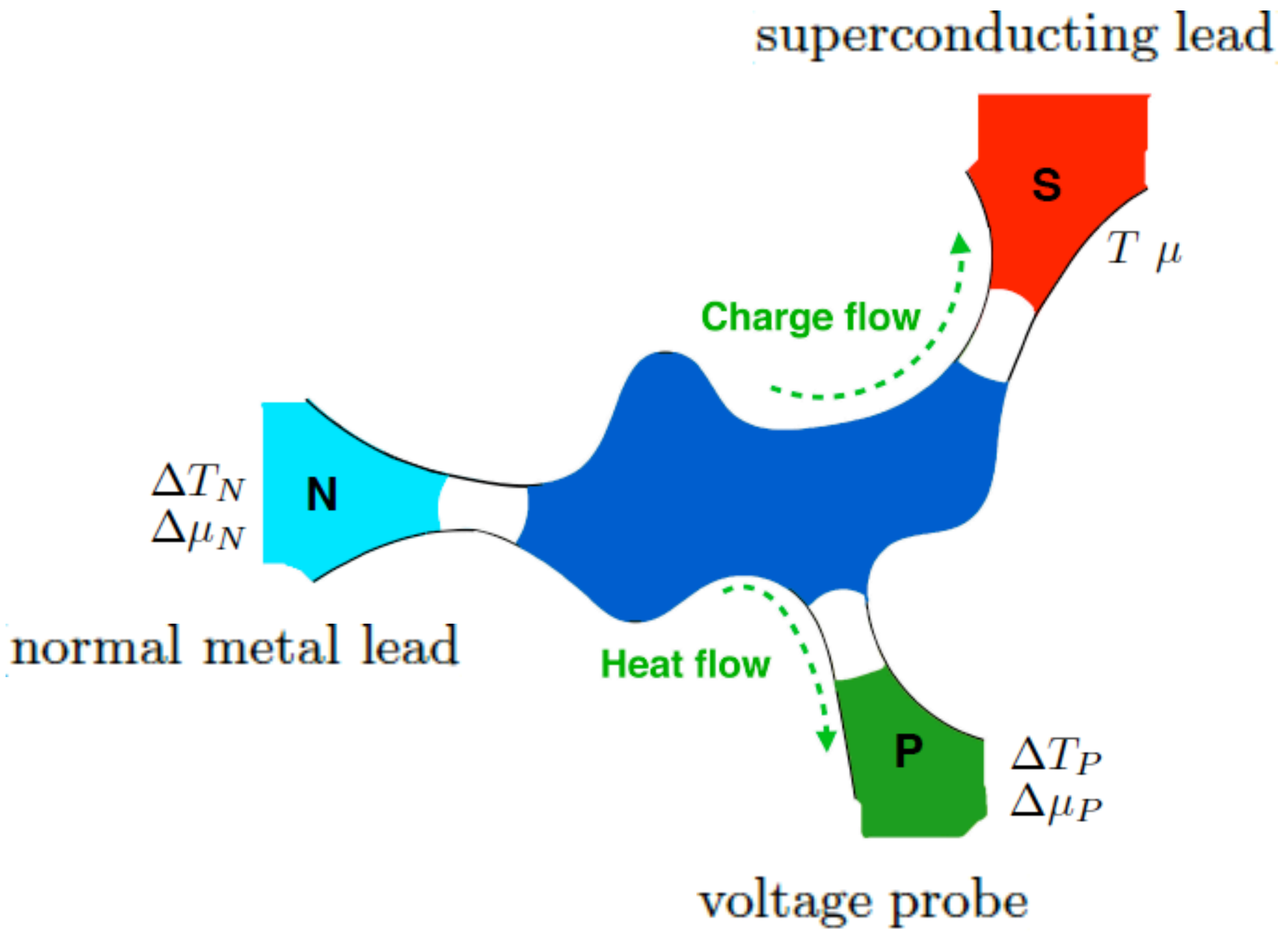
Illustrative example: double dot





In this simple model non-local thermopowers are different from zero

Heat-charge separation



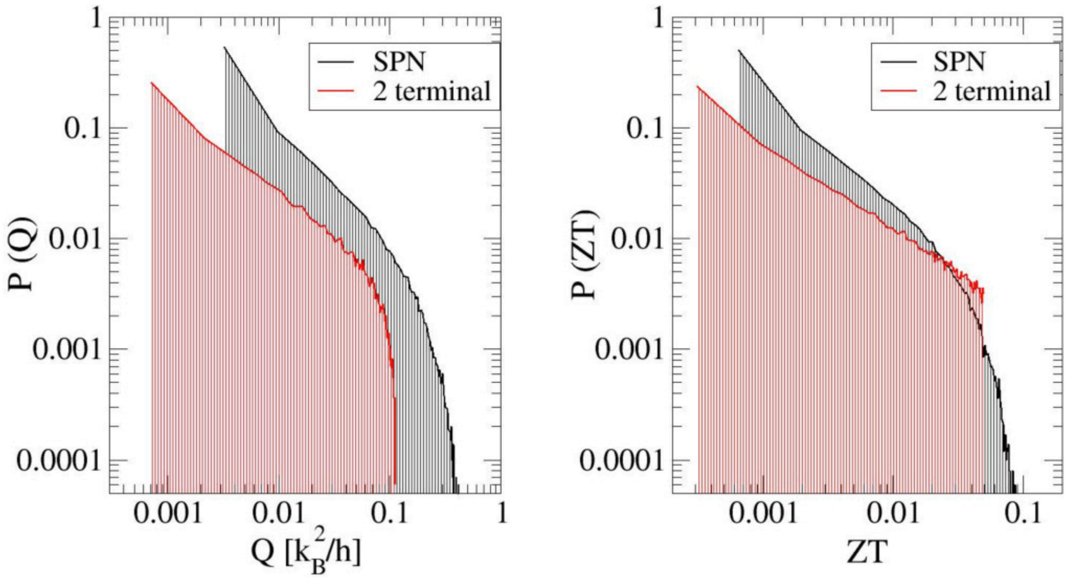
(F. Mazza, S. Valentini, R. Bosisio, G.B.,
R. Fazio, V. Giovannetti, F. Taddei, PRB 91, 245435 (2015))

Improved thermoelectric performances

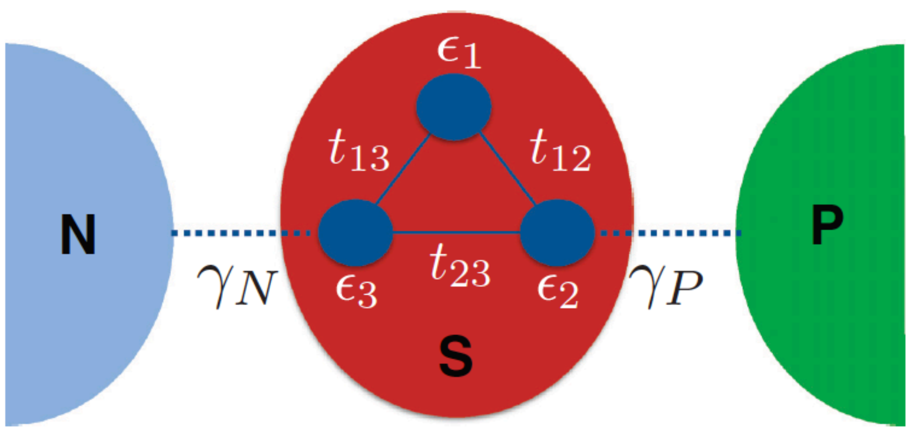
Statistics of scattering matrices (within the Sommerfeld regime)

Power factor

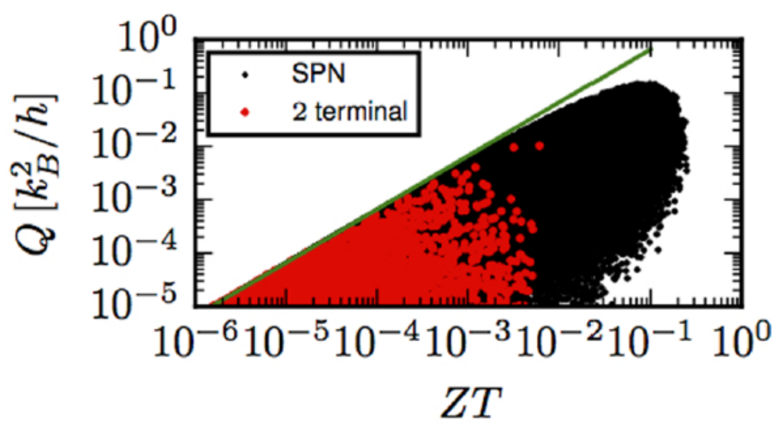
$$Q = GS^2$$



Tridot model



GOE Hamiltonian



Summary for multiterminal thermoelectricity

The third terminal can be useful to improve the thermoelectric performances of a system with respect to the two-terminal case

Possible extensions:
- systems with a magnetic field breaking time-reversibility,
- bosonic terminals,
- interacting systems

Cyclic thermal machines

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

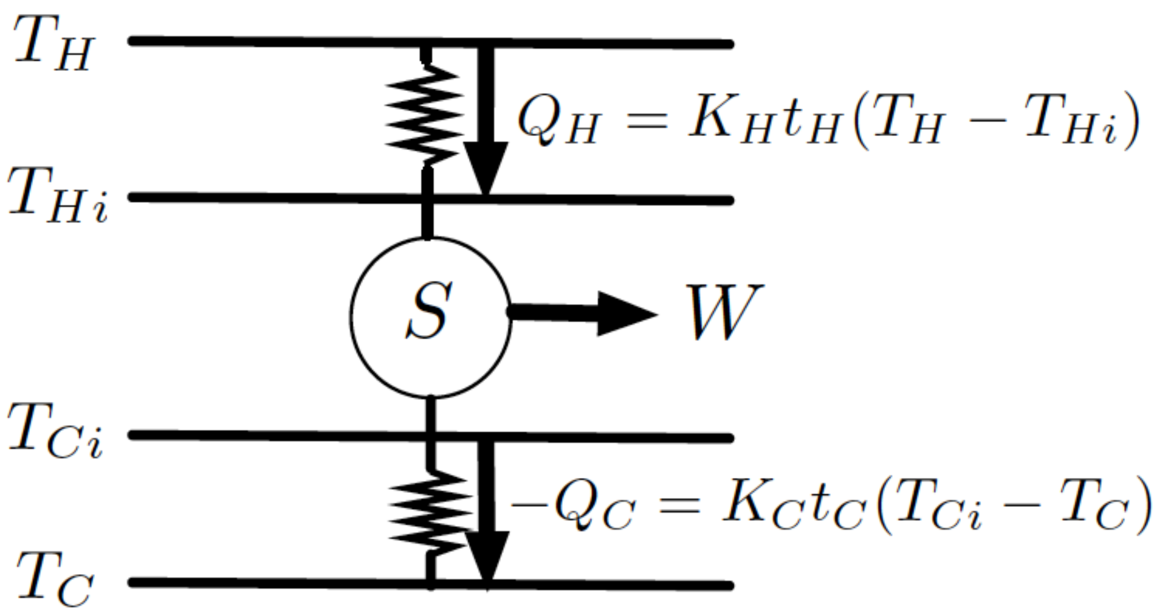
$$\eta = \frac{W}{Q_H} \leq \eta_C = 1 - \frac{T_C}{T_H} \qquad (T_H > T_C)$$

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

The ideal Carnot engine is a reversible machine, since there is no dissipation to ensure causality

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

$$\begin{aligned} \alpha &= T_H - T_{Hi} \\ \beta &= T_{Ci} - T_C \end{aligned}$$

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

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

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

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

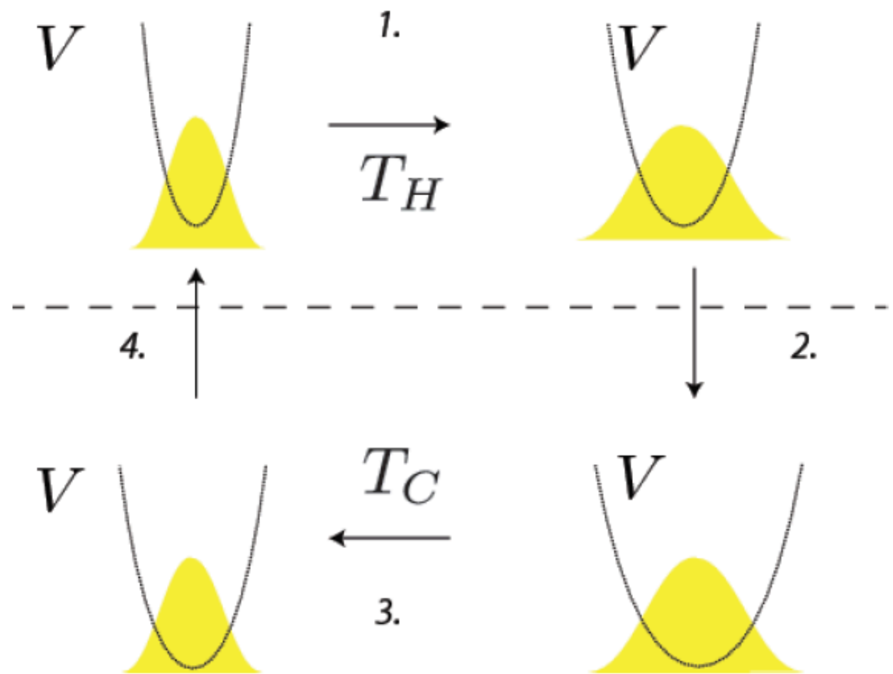
[Yvon, 1955; Chambadal, 1957; Novikov, 1958; Curzon and Ahlborn, Am. J. Phys. 43, 22 (1975)]

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



Time-dependent trapping potential $V(x,\lambda(t))$

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: $\eta_{CA} = \dfrac{\eta_C}{2}$

Low-dissipation engines

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

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

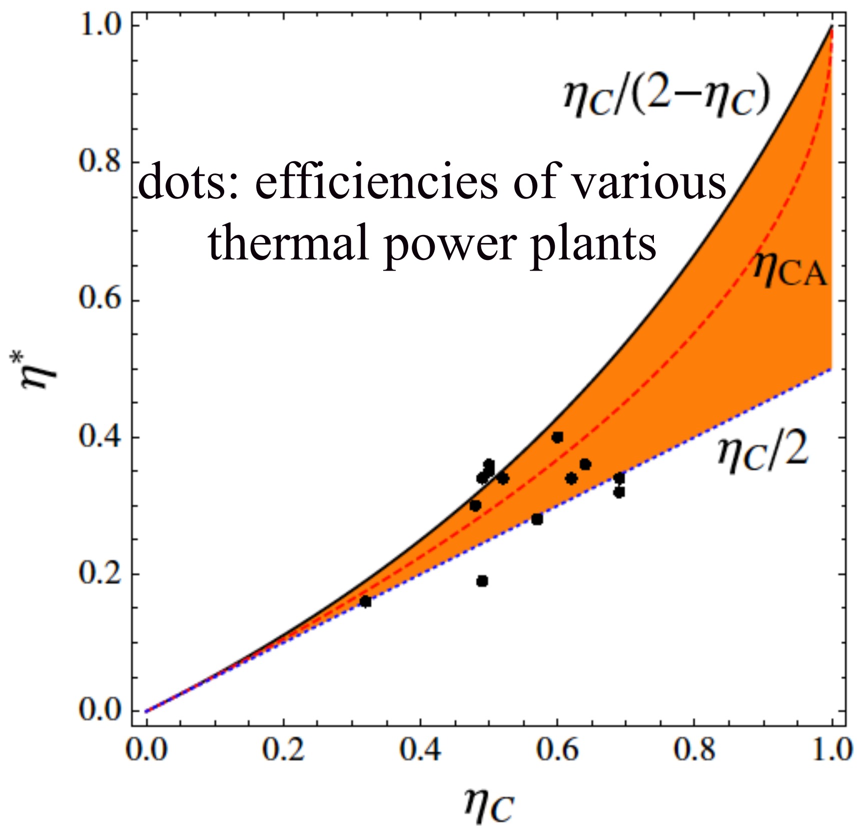
$$P = \frac{Q_H + Q_C}{t_H + t_C} = \frac{(T_H - T_C)\Delta\mathscr{S} - T_H\Sigma_H/t_H - T_C\Sigma_C/t_C}{t_H + t_C}$$

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

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

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

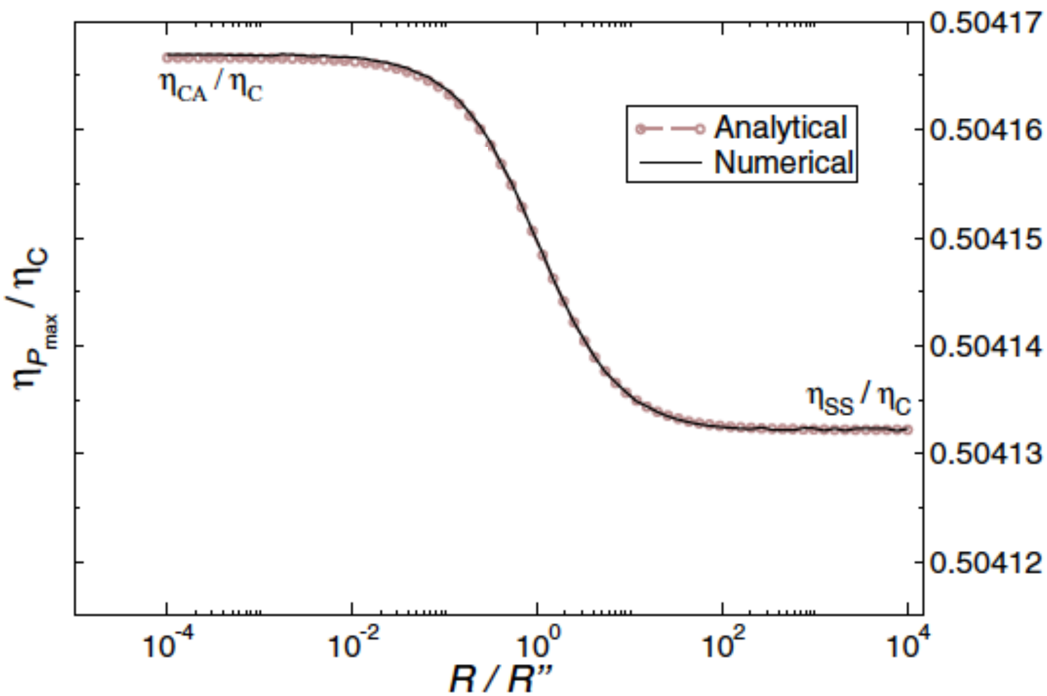
The CA limit is recovered for symmetric dissipation: $\Sigma_H = \Sigma_C$



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

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)]

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?

Investigate time-dependent driving