Fundamental Aspects of Steady State Heat to Work Conversion

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OUTLINE

Coupled charge and heat flow: a dynamical system's perspective on a fundamental problem of statistical physics

Can we learn something about microscopic <u>mechanisms</u> leading to high energy conversion (thermoelectric) efficiency from the study of <u>nonlinear dynamical systems</u>?

Part I: Interacting momentum-conserving systems

Part II: Systems with time-reversal symmetry breaking: Asymmetric thermopower; Overcoming the Curzon-Ahlborn limit; Magnetic thermal switch

Part III: Multi-terminal systems: heat-charge separation

Volta and the discovery of thermoelectricity

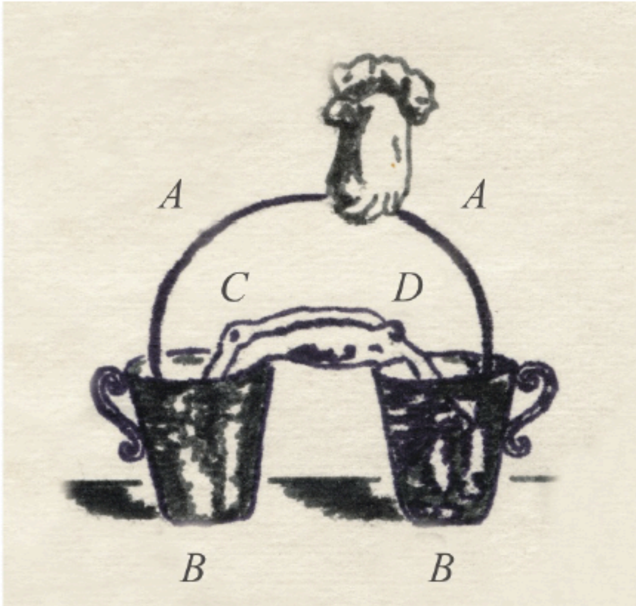


Fig. 3 Schematic of Volta's experiment that resulted in the discovery of thermoelectricity: A – metal (iron) arc; B – glasses with water; C and D – frog parts placed in the glasses with water.

(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...*"

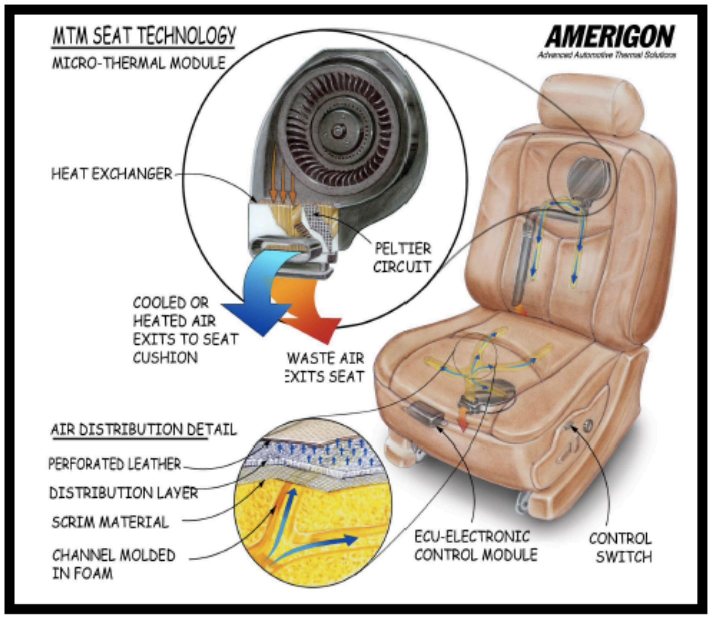
Abram Ioffe (1950s): Doped semiconductors have large thermoelectric effect

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

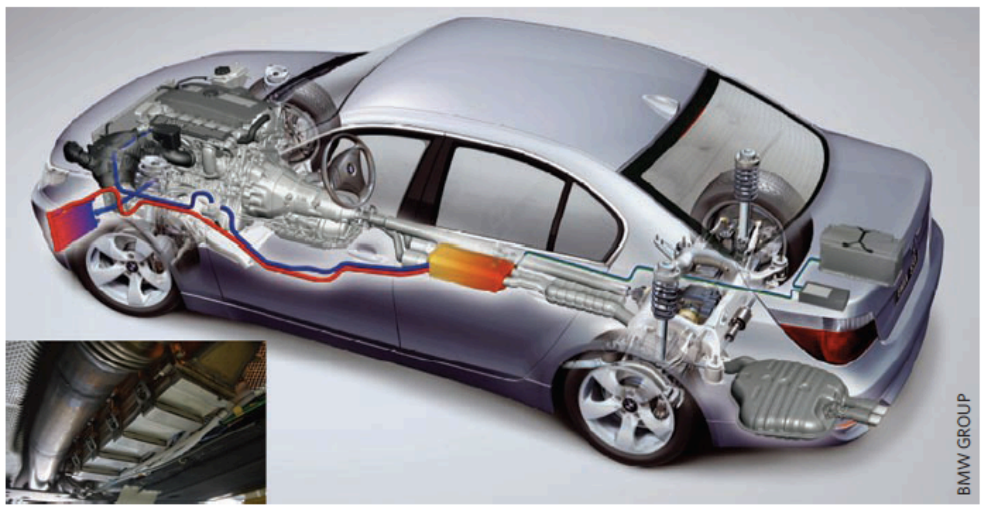


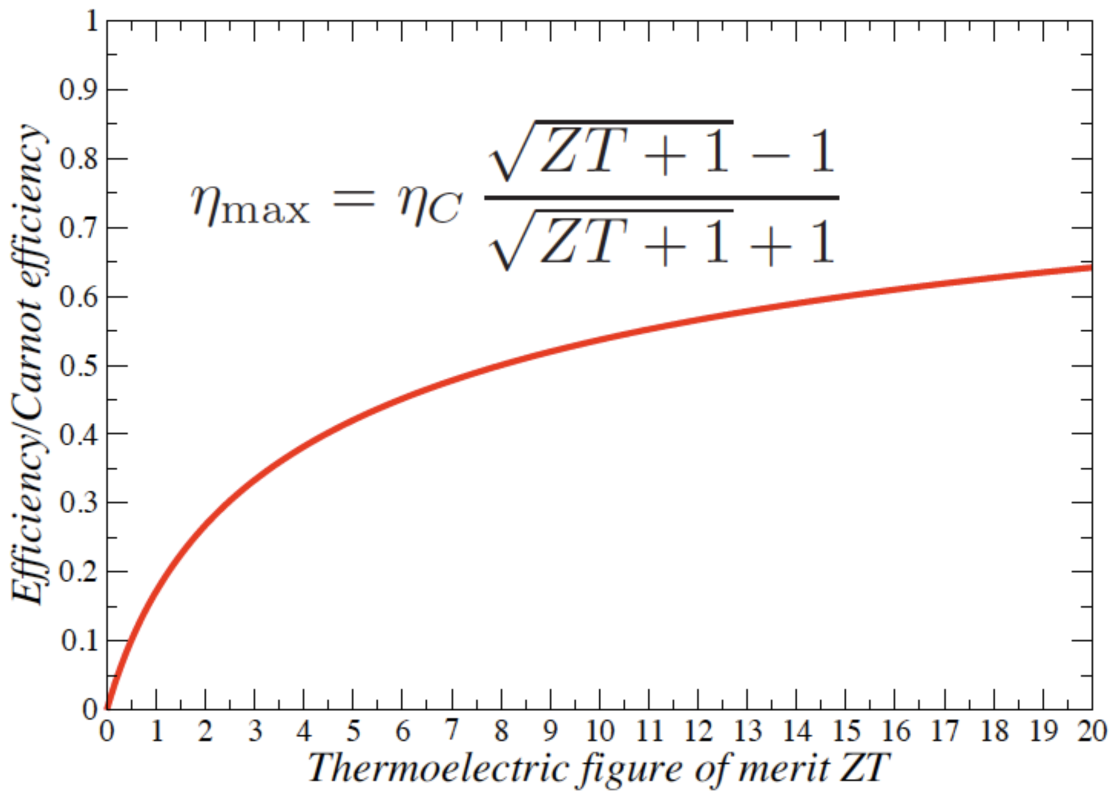
Figure 1 | Integrating thermoelectrics into vehicles for improved fuel efficiency. Shown is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue).

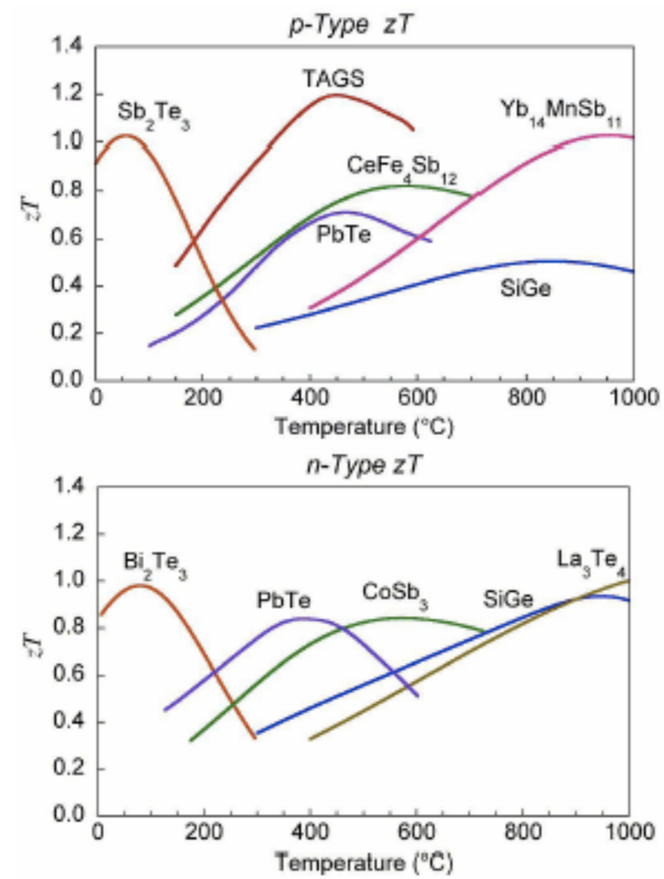
Mildred Dresselhaus et al. (Adv. Materials, 2007):

“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





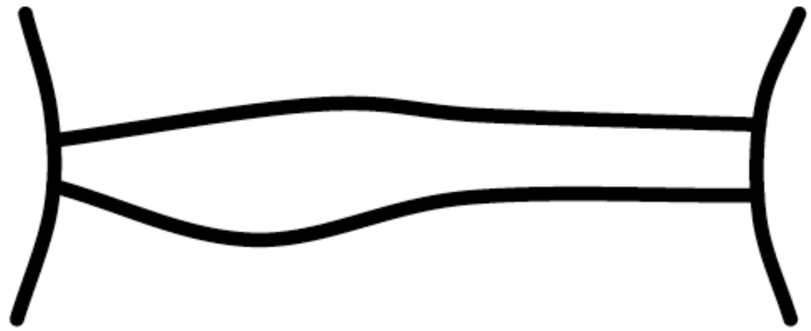
Cronin Vining: *limited role for thermoelectrics in the climate crisis (ZT too small to replace mechanical engines for large-scale applications)*

Arun Majumdar: at issue are some fundamental scientific challenges, which could be overcome by deeper understanding of charge and heat transport...

Coupled 1D particle and heat transport

Stochastic baths: ideal gases at fixed temperature and chemical potential

T_L μ_L



T_R μ_R

$$\begin{cases} J_\rho = L_{\rho\rho} X_1 + L_{\rho q} X_2 \\ J_q = L_{q\rho} X_1 + L_{qq} X_2 \end{cases}$$

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

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

$$\beta = 1/T$$

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

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

$$\Delta T = T_L - T_R$$

Onsager relation:

$$L_{\rho q} = L_{q\rho}$$

Positivity of entropy production:

$$L_{\rho\rho} \geq 0, \quad L_{qq} \geq 0, \quad \det \mathbf{L} \geq 0$$

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

Onsager and transport coefficients

$$G = \left(\frac{J_\rho}{\Delta\mu/e}\right)_{\Delta T=0} \Rightarrow \quad G = \frac{e^2}{T} L_{\rho\rho}$$

$$\Xi = \left(\frac{J_q}{\Delta T}\right)_{J_\rho=0} \Rightarrow \quad \Xi = \frac{1}{T^2}\frac{\det \mathbf{L}}{L_{\rho\rho}}$$

$$S = -\left(\frac{\Delta\mu/e}{\Delta T}\right)_{J_\rho=0} \Rightarrow S = \frac{1}{eT}\frac{L_{\rho q}}{L_{\rho\rho}}$$

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

Maximum efficiency

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

Find the maximum of η over X_1, for fixed X_2 (i.e., over the applied voltage ΔV for fixed temperature difference ΔT)

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

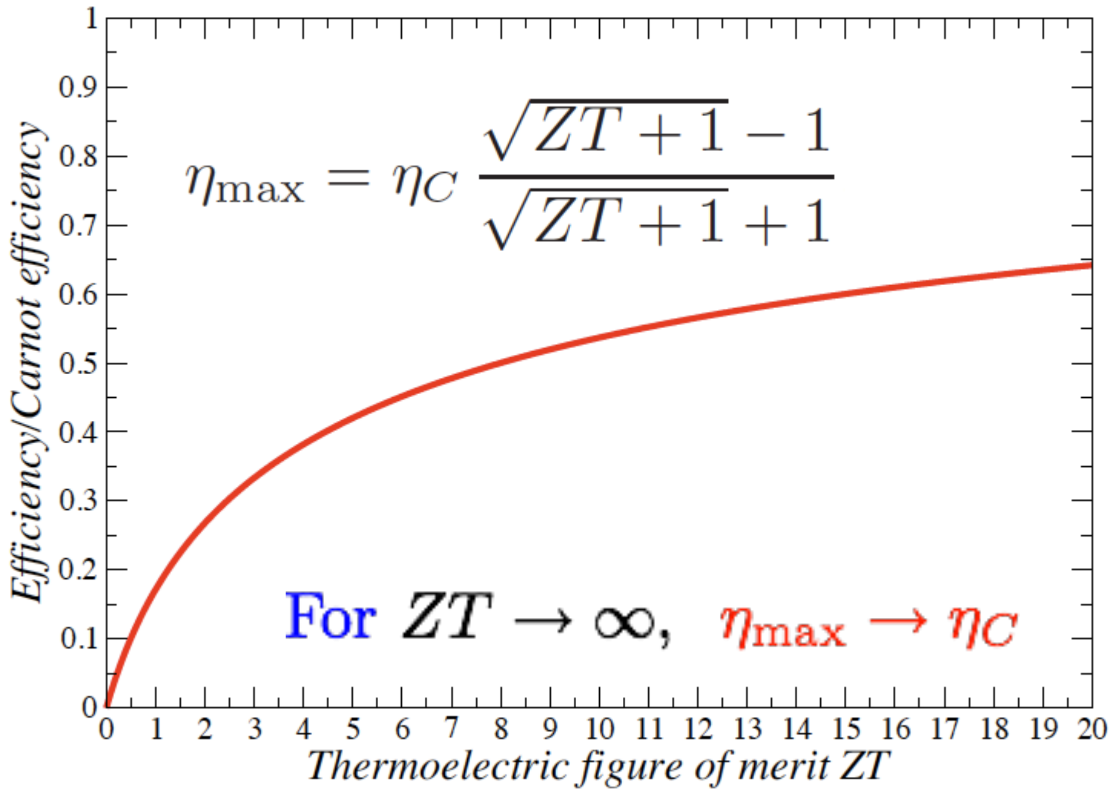
Maximum efficiency (for system with time-reversal symmetry)

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

Thermoelectric figure of merit

$$ZT = \frac{L_{q\rho}^2}{\det \mathbf{L}} = \frac{GS^2}{\Xi} T$$

Positivity of entropy production implies $ZT > 0$



Efficiency at maximum power

Output power $\omega = -TX_1(L_{\rho\rho}X_1 + L_{\rho q}X_2)$

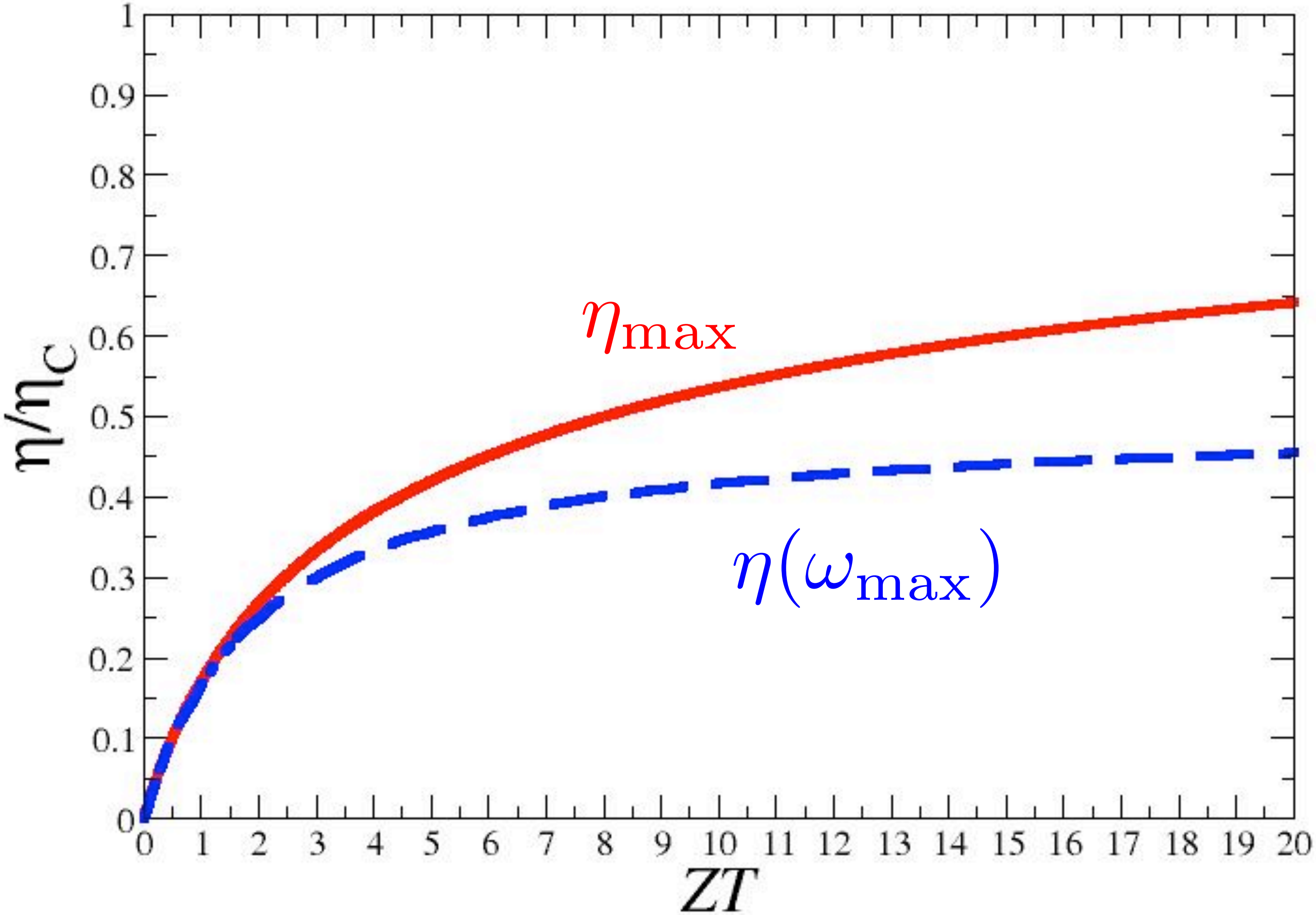
Find the maximum of ω over X_1, for fixed X_2 (over the applied voltage ΔV for fixed ΔT)

Maximum achieved for $$X_1 = -\frac{L_{\rho q}}{2L_{\rho\rho}} X_2$$

Efficiency at maximum power

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

η_{CA} Curzon-Ahlborn upper bound



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

ZT diverges iff the Onsager matrix is ill-conditioned, that is, the condition number:

$$\mathrm{cond}(\mathbf{L}) \equiv \frac{[\mathrm{Tr}(\mathbf{L})]^2}{\det(\mathbf{L})}$$ **diverges**

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

$$J_q \propto J_\rho$$

(the ratio J_q/J_ρ is independent of the applied voltage and temperature gradients)

Non-interacting systems, Landauer-Büttiker 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 reservoir α

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

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

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

Thermoelectric efficiency

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

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

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

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)]

Is energy-filtering necessary to get Carnot efficiency?

No, for interacting systems with momentum conservation

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

$$L_{ij} = \lim_{\omega \to 0} \mathrm{Re} L_{ij}(\omega)$$

$$L_{ij}(\omega) = \lim_{\epsilon \to 0} \int_0^\infty dt e^{-i(\omega - i\epsilon)t} \lim_{\Lambda \to \infty} \frac{1}{\Lambda} \int_0^\beta d\tau \langle J_i J_j(t + i\tau) \rangle_T$$

$$\mathrm{Re} L_{ij}(\omega) = 2\pi \mathcal{D}_{ij} \delta(\omega) + L_{ij}^{\mathrm{reg}}(\omega)$$

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

$$D_{ij}(\Lambda) \equiv \frac{1}{2\Lambda} \lim_{t\to\infty} \frac{1}{t} \int_0^t dt' \langle J_i(t') J_j(0) \rangle_T = \frac{1}{2\Lambda} \sum_{n=1}^{M} \frac{\langle J_i Q_n \rangle_T \langle J_j Q_n \rangle_T}{\langle Q_n^2 \rangle_T}$$

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

$$\mathcal{D}_{ij} = \lim_{t\to\infty} \lim_{\Lambda\to\infty} \frac{1}{2\Lambda t} \int_0^t dt' \langle J_i(t') J_j(0) \rangle_T$$

Assuming commutativity of the two limits,

$$\mathcal{D}_{ij} = \lim_{\Lambda\to\infty} D_{ij}(\Lambda)$$

Momentum-conserving systems

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

Ballistic contribution to det*(L)* vanishes as

$$\mathcal{D}_{\rho\rho}\mathcal{D}_{uu} - \mathcal{D}_{\rho u}^2 = 0$$

$$k \propto \frac{\det \mathbf{L}}{L_{\rho\rho}} \propto \Lambda^{\alpha}, \quad \alpha < 1$$

$$\sigma \propto L_{\rho\rho} \propto \Lambda$$

$$ZT = \frac{\sigma S^2}{\kappa} T \propto \Lambda^{1-\alpha} \to \infty \text{ when } \Lambda \to \infty$$

$$S \propto \frac{L_{\rho q}}{L_{\rho\rho}} \propto \Lambda^0$$

(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

$$D_{\rho\rho} D_{uu} - D_{\rho u}^2 = \| \boldsymbol{x}_\rho \|^2 \| \boldsymbol{x}_u \|^2 - \langle \boldsymbol{x}_\rho , \boldsymbol{x}_u \rangle^2 \geqslant 0$$

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

$$\langle \boldsymbol{x}_\rho, \boldsymbol{x}_u \rangle = \sum_{k=1}^{M} x_{\rho k} x_{uk}$$

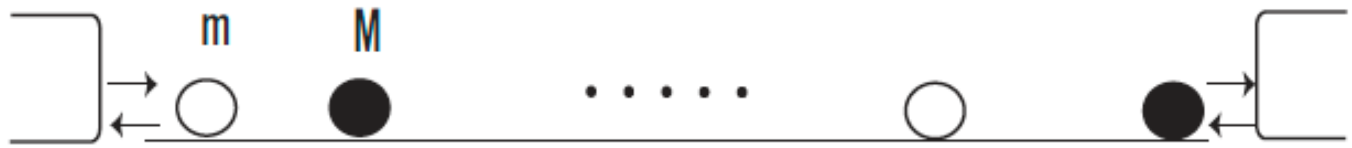
Equality arises only in the exceptional case when the two vectors are parallel; in general

$$\det \mathbf{L} \propto L^2, \ \kappa \propto \Lambda, \ ZT \propto \Lambda^0$$

Example: 1D interacting classical gas

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

T_L
μ_L



T_R
μ_R

For $M = m$

(integrable model)

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

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

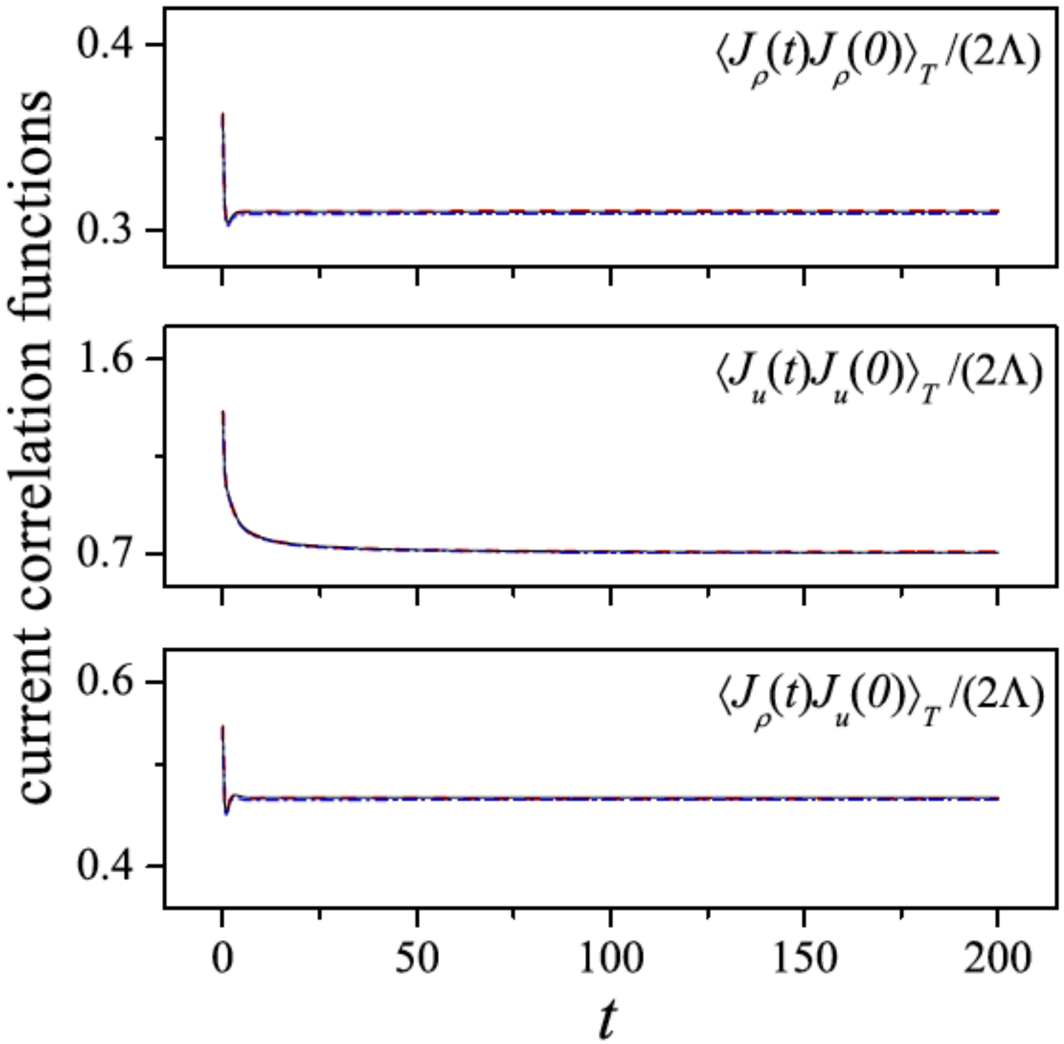
$ZT = 1$ (at $\mu = 0$)

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

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),

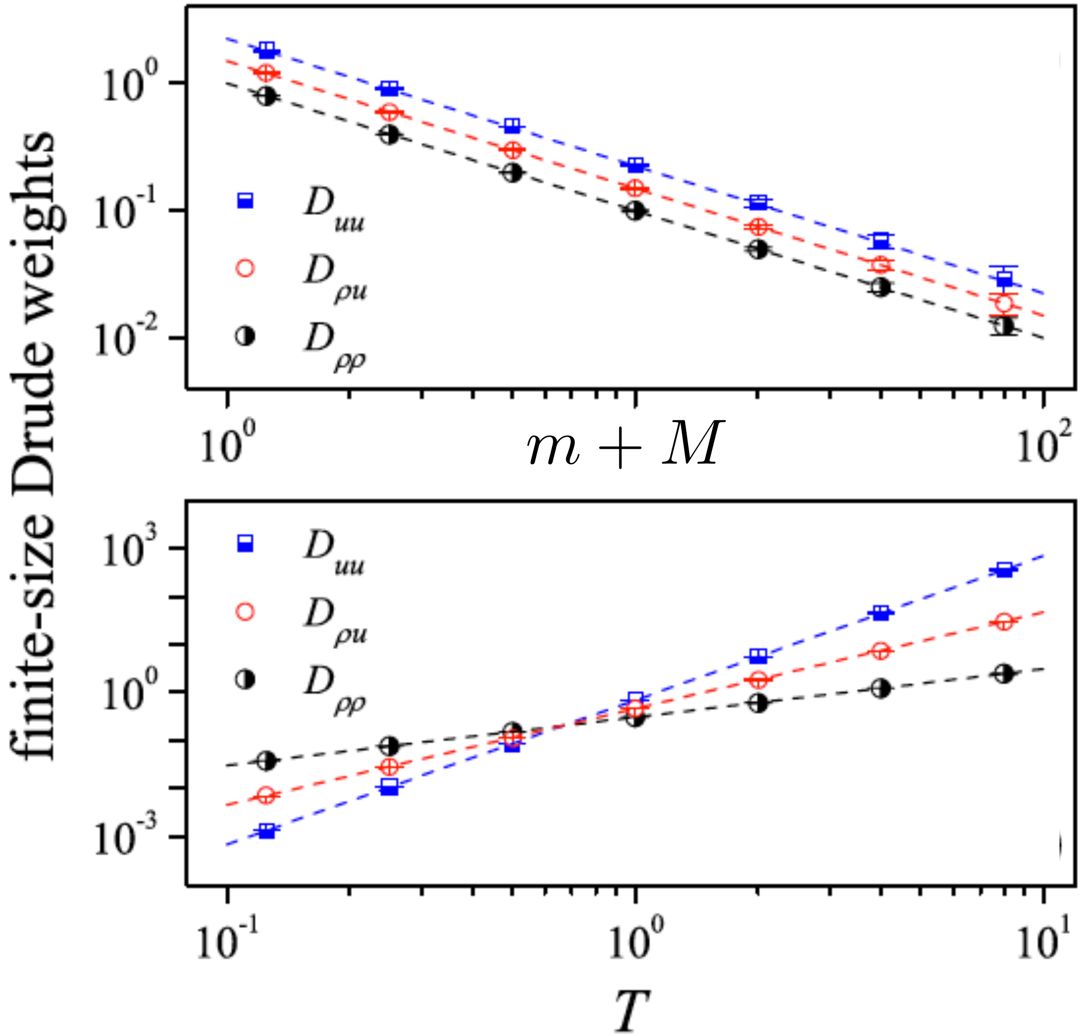
and 1024 (black solid curve)

Finite-size Drude weights: analytical results vs. numerics

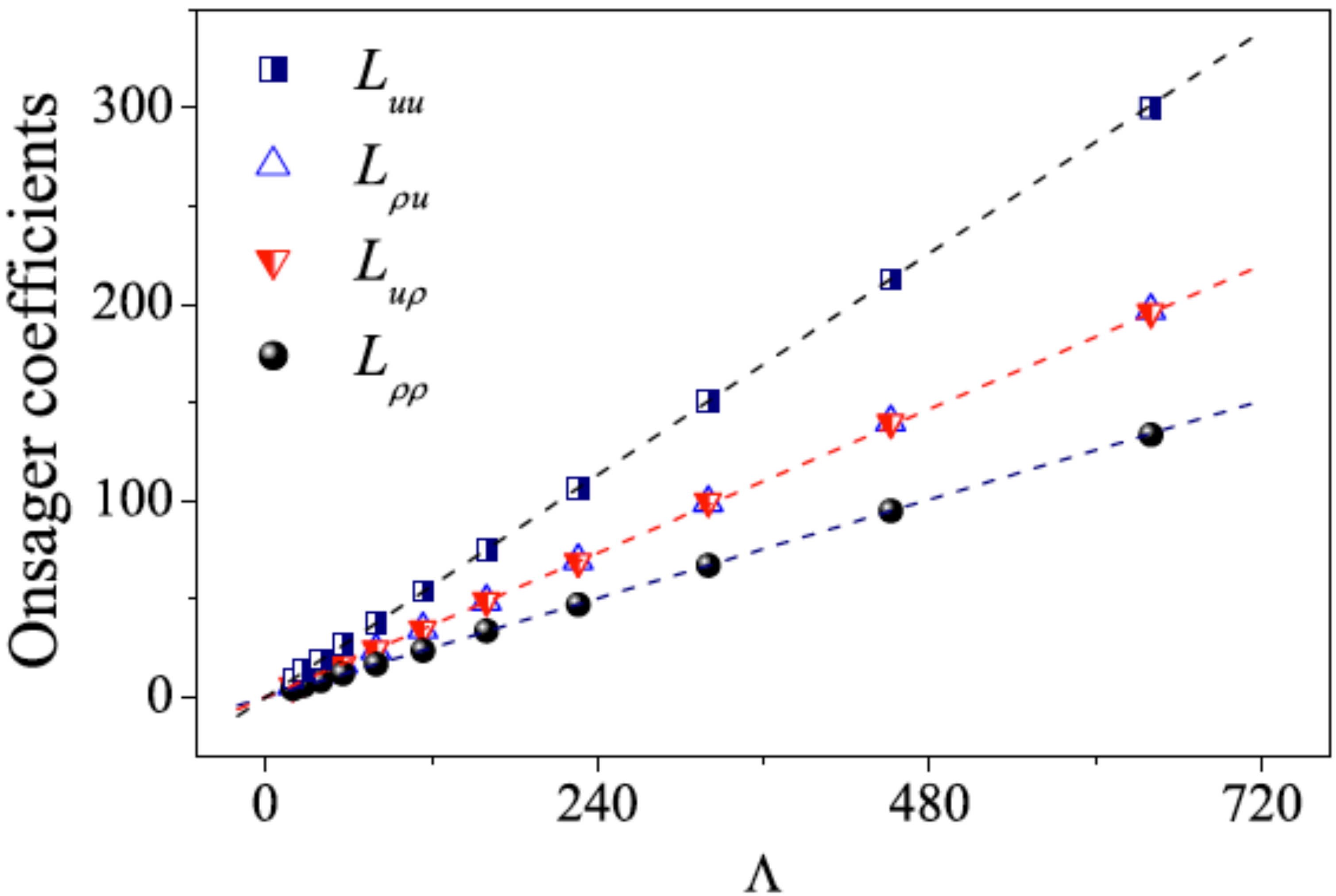
$$D_{\rho\rho}(\Lambda) = \frac{TN^2}{2\Lambda(mN_1 + MN_2)},$$

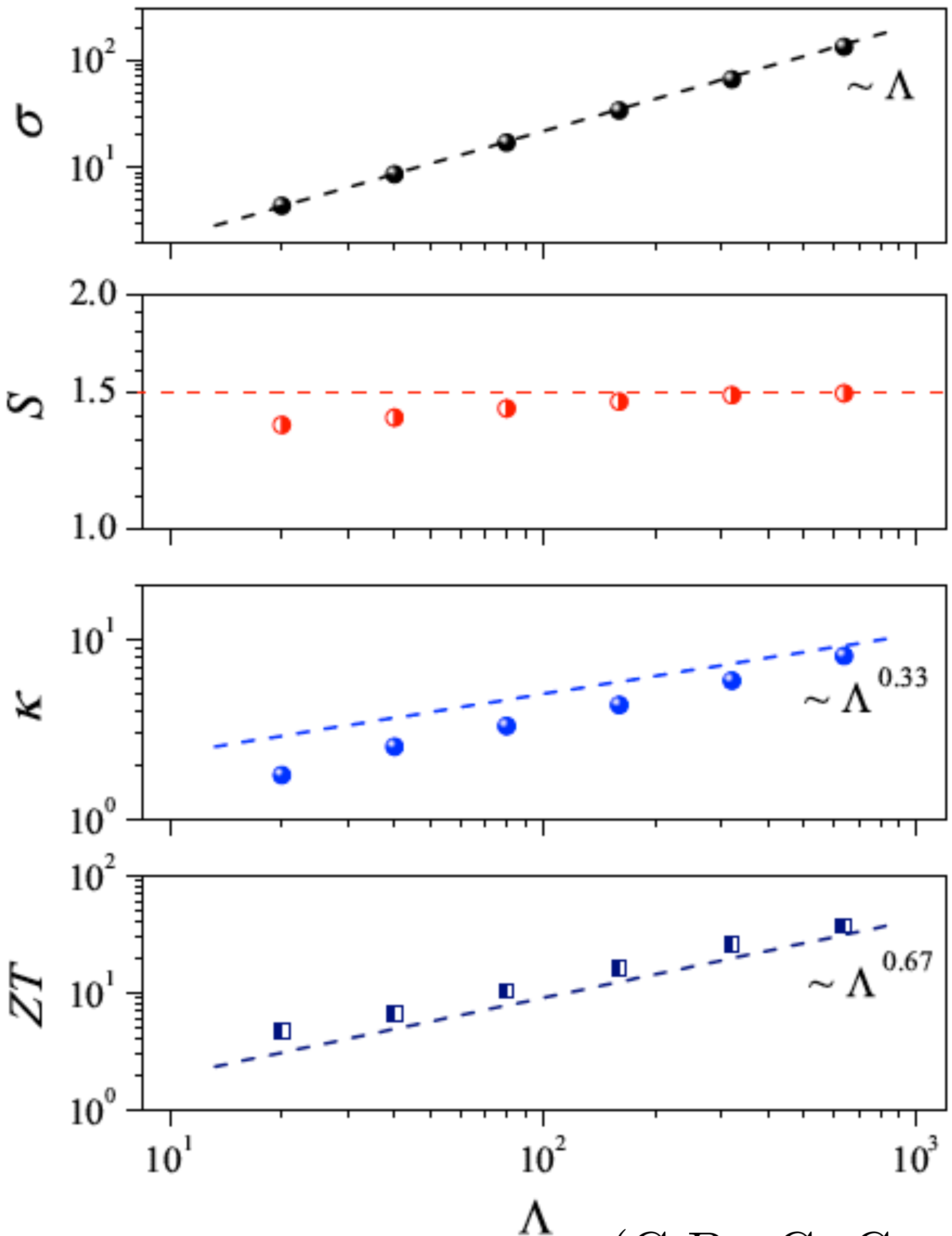
$$D_{uu}(\Lambda) = \frac{9T^3N^2}{8\Lambda(mN_1 + MN_2)},$$

$$D_{\rho u}(\Lambda) = \frac{3T^2N^2}{4\Lambda(mN_1 + MN_2)}.$$



Ballistic behavior of Onsager coefficients





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?

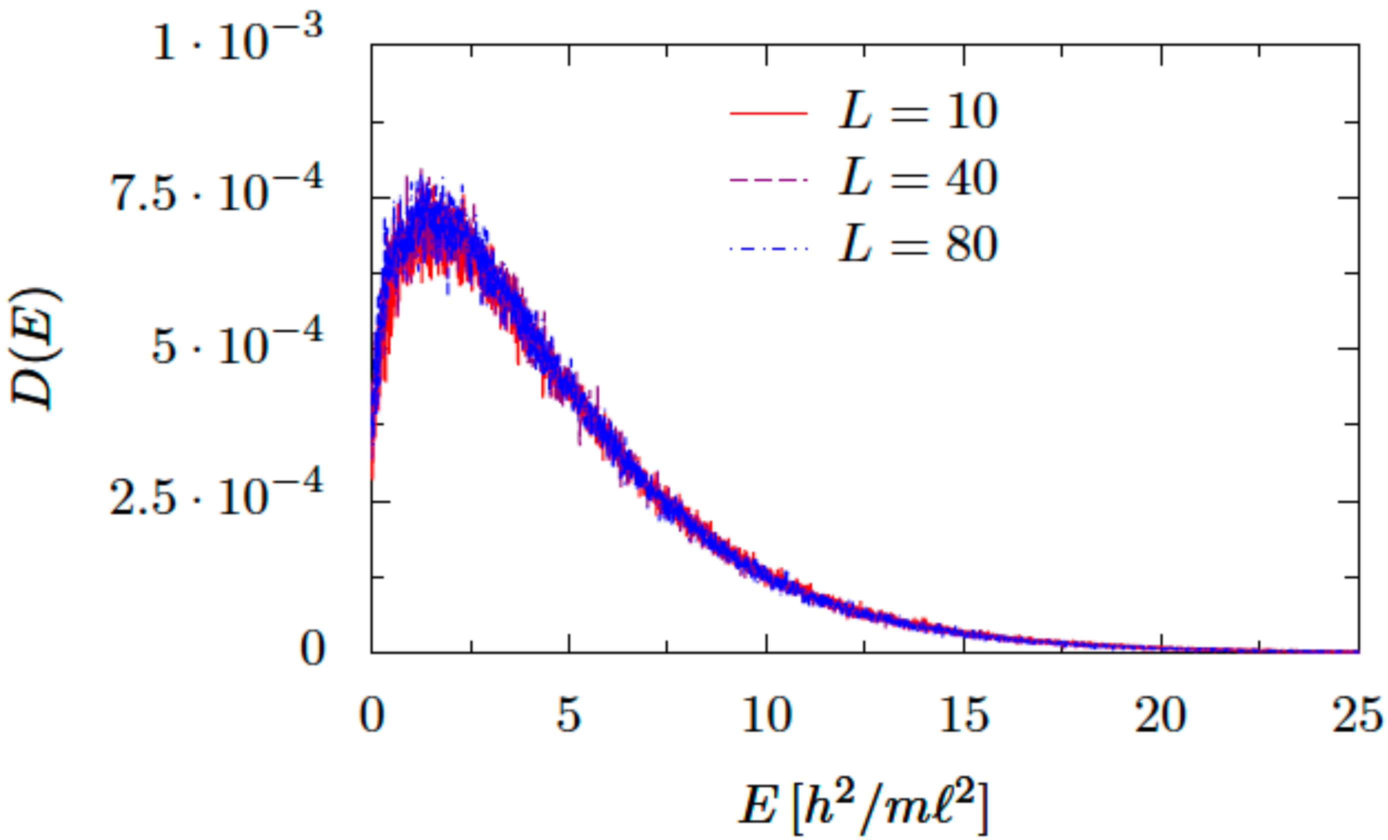
At a given position x compute:

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

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

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

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



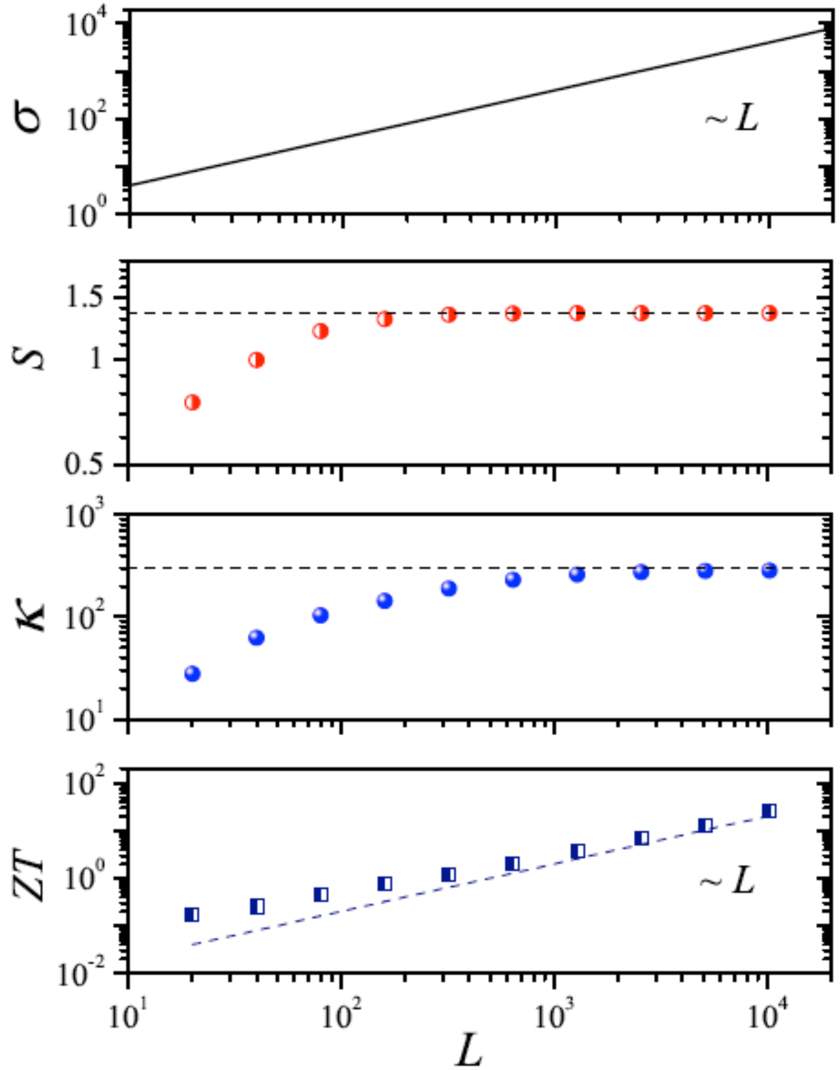
There is no sign of narrowing of D(E) with increasing the system size L

A mechanism for increasing ZT different from energy filtering is needed

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

1D 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., preprint)

Multiparticle collision dynamics (Kapral model)

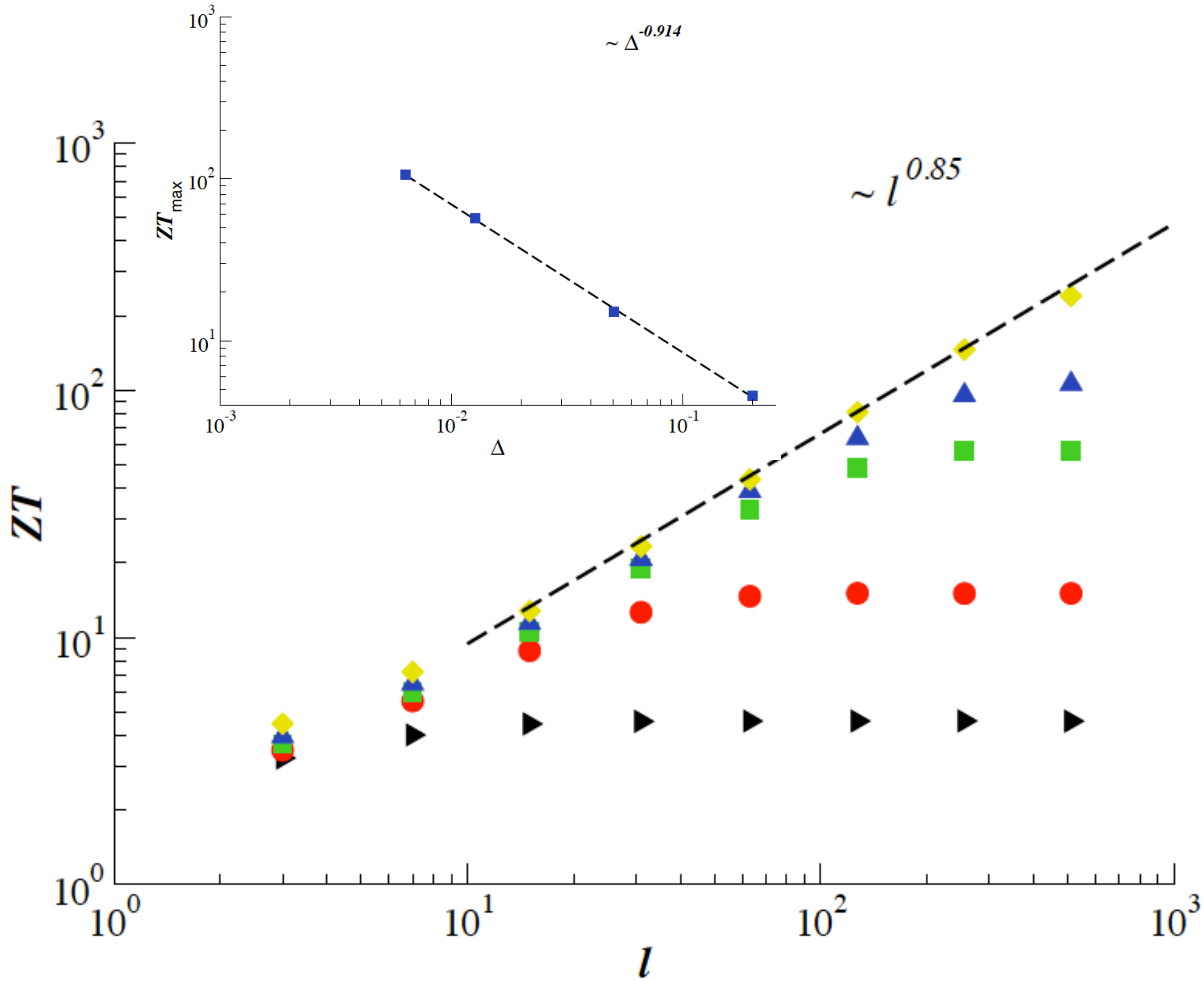
Streaming step: free propagation during a time τ

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

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

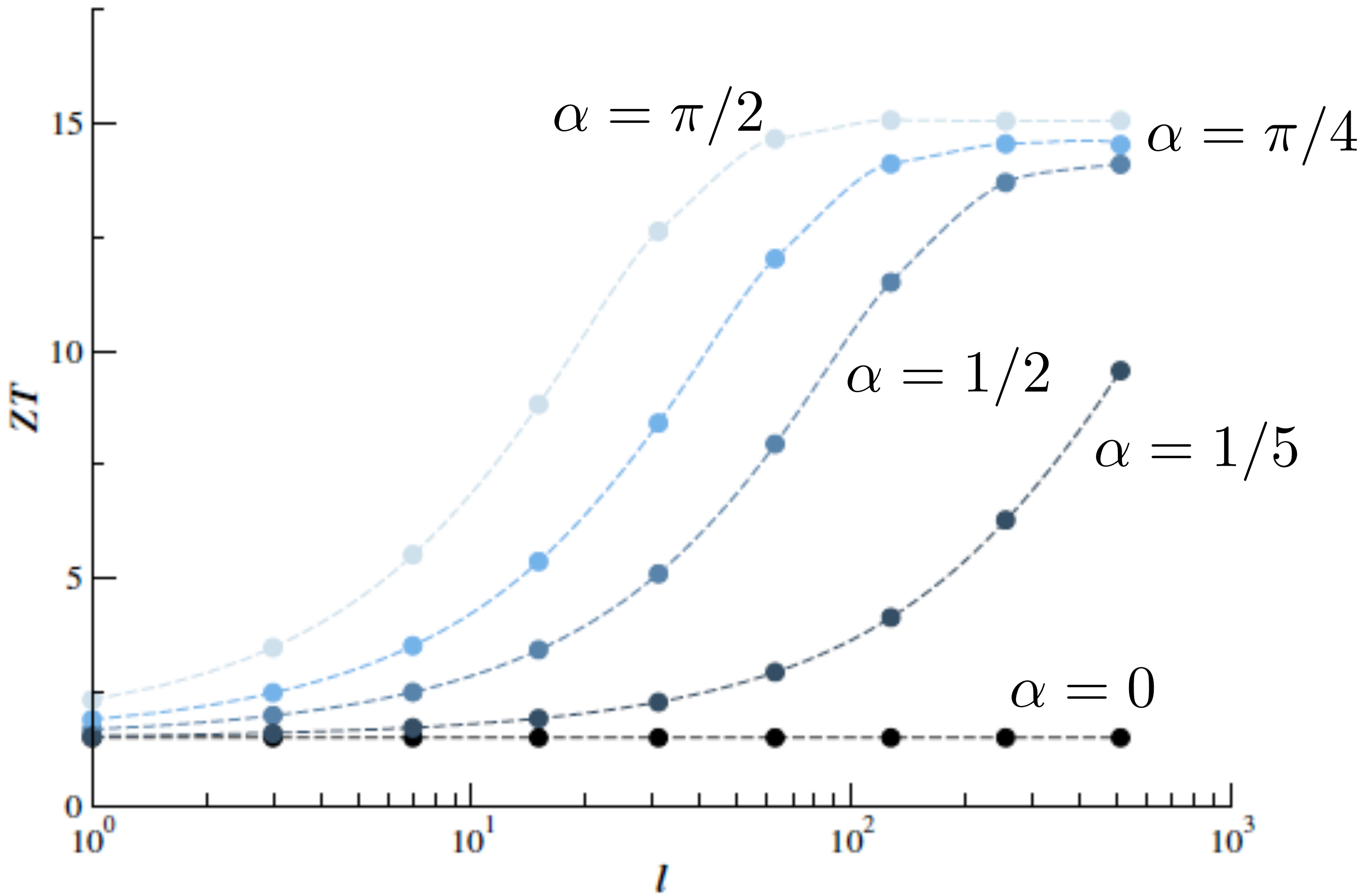
$$\vec{v}_i \longrightarrow \vec{V}_{\mathrm{CM}} + \hat{\mathcal{R}}^{\pm\alpha} \left(\vec{v}_i - \vec{V}_{\mathrm{CM}} \right)$$

Momentum is conserved



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

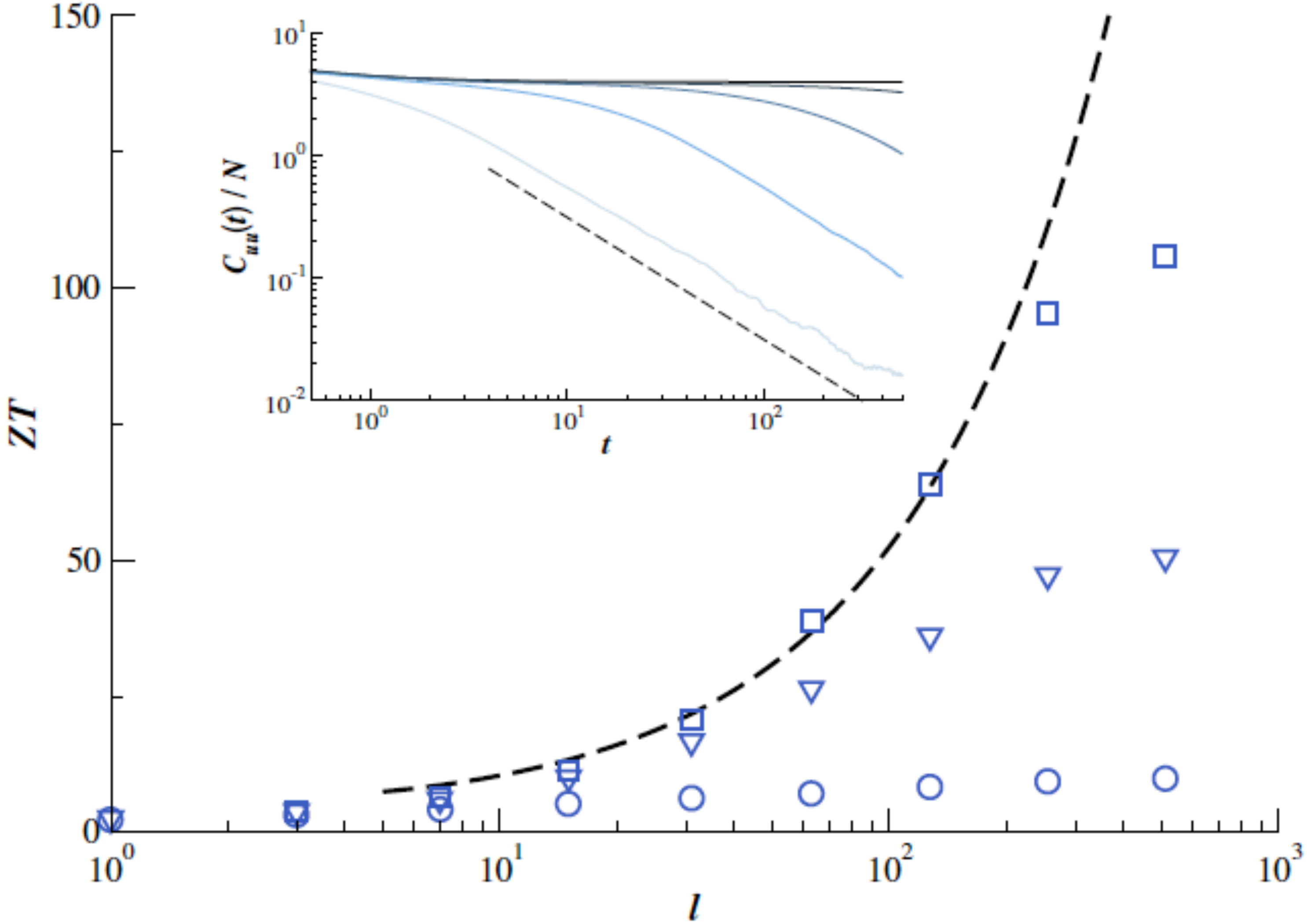
2D simulations (Kapral model)



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

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)

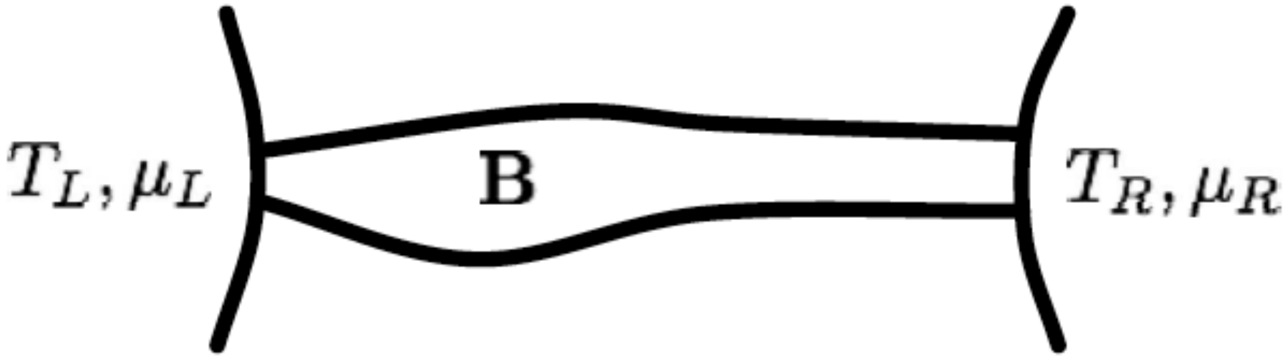
2) Absence of dissipative channels

Mechanism fundamentally different from energy filtering

No dimensionality restrictions, argument applicable also to quantum systems

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

And when time-reversal is broken?



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

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

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

$$\beta = 1/T$$

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

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

$$\Delta T = T_L - T_R$$

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

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

Constraints from thermodynamics

POSITIVITY OF THE ENTROPY PRODUCTION:

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

ONSAGER-CASIMIR RELATIONS:

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

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

EFFICIENCY AT MAXIMUM POWER

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

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

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

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

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

Efficiency at maximum power depends on two parameters

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

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

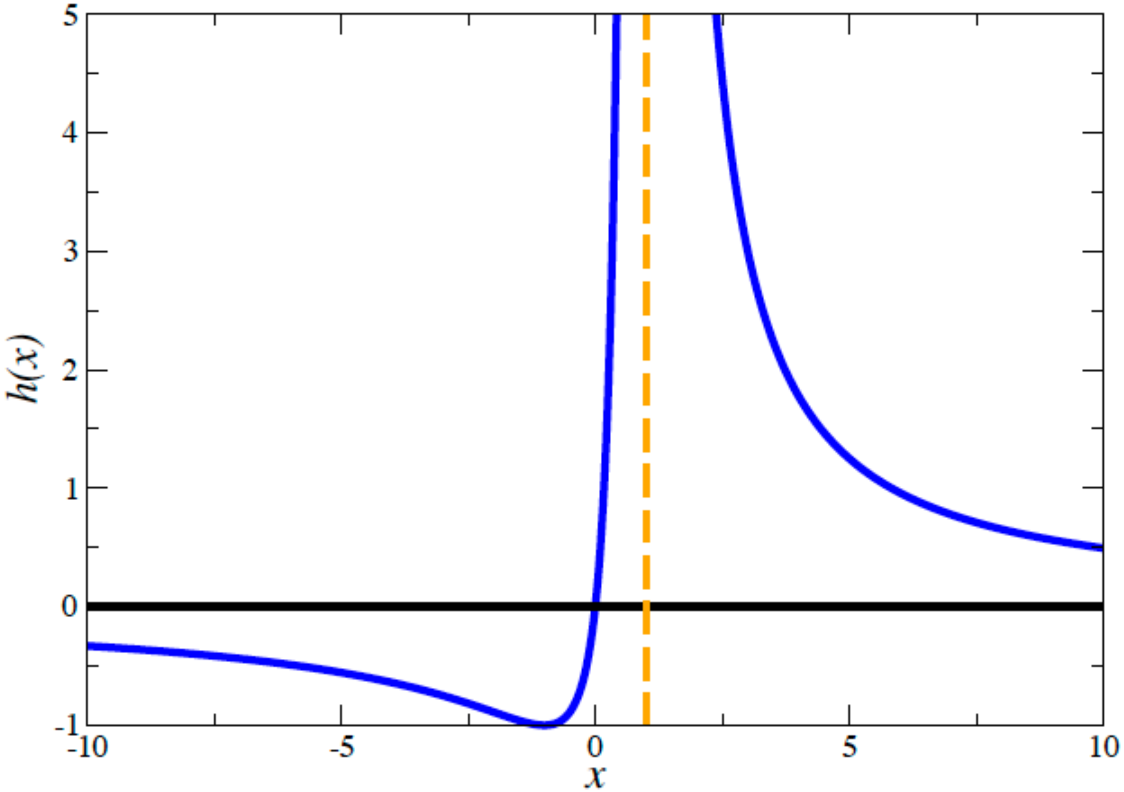
$$\eta(\omega_{\max}) = \frac{\eta_C}{2} \frac{xy}{2+y}$$

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

asymmetry parameter $x = 1$

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

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



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

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

achieved for $y = h(x)$

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

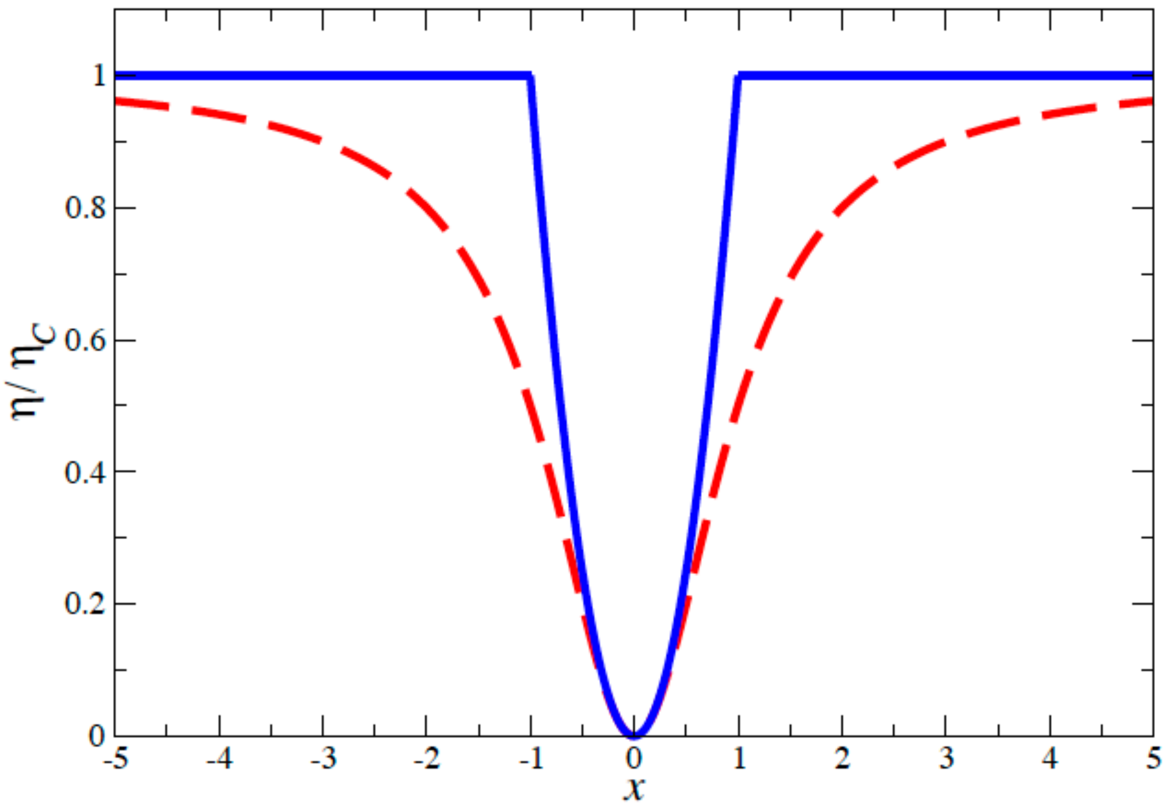
MAXIMUM EFFICIENCY

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

Maximum efficiency achieved for

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

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



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 strong coupling condition</u>

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

OUTPUT POWER AT MAXIMUM EFFICIENCY

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

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

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

Reversible part of the currents

$$J_i^{\mathrm{rev}} \equiv \frac{L_{ij} - L_{ji}}{2} X_j, \quad i = \rho, q$$

$$J_i^{\mathrm{irr}} \equiv L_{ii} X_i + \frac{L_{ij} + L_{ji}}{2} X_j$$

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

$$\dot{S} = J_\rho X_1 + J_q X_2 = J_\rho^{\mathrm{irr}} X_1 + J_q^{\mathrm{irr}} X_2$$

Possibility of dissipationless transport?

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

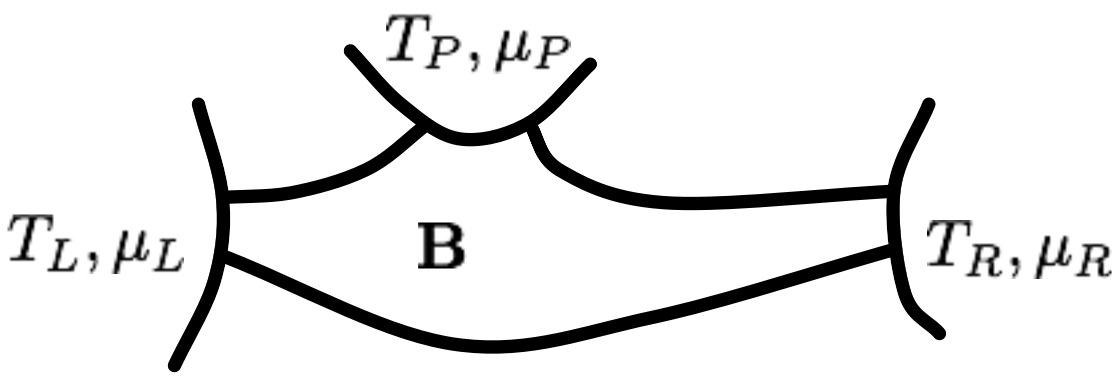
How to obtain asymmetry in the Seebeck coefficient?

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).

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

Entropy production (linear response):

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

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

Three-terminal Onsager matrix

Equation connecting fluxes and thermodynamic forces:

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

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

In block-matrix form:

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

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

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

Two-terminal Onsager matrix for partially coherent transport

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

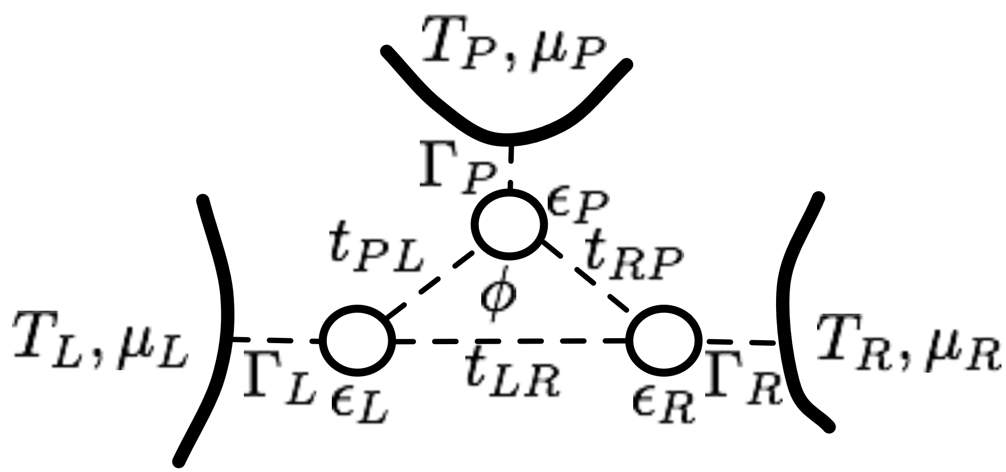
$$\boldsymbol{J}_\alpha = \boldsymbol{L}_{\alpha\alpha}{}' \boldsymbol{X}_\alpha, \quad \boldsymbol{L}_{\alpha\alpha}{}' \equiv \left(\boldsymbol{L}_{\alpha\alpha} - \boldsymbol{L}_{\alpha\beta} \boldsymbol{L}_{\beta\beta}{}^{-1} \boldsymbol{L}_{\beta\alpha}\right)$$

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

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

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

Illustrative three-dot example

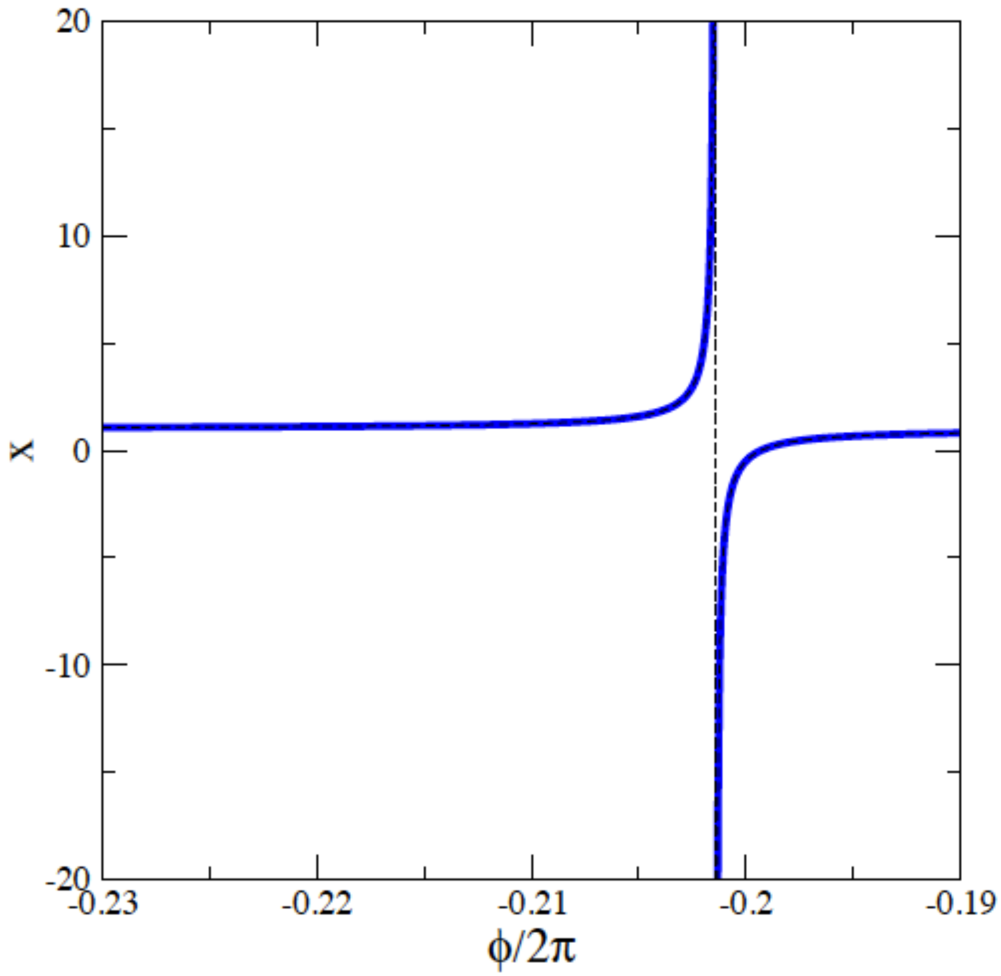


$$H_S = \sum_k \epsilon_k c_k^\dagger c_k + (t_{LR} c_R^\dagger c_L e^{i\phi/3} + t_{RP} c_P^\dagger c_R e^{i\phi/3} + t_{PL} c_L^\dagger c_P e^{i\phi/3} + \text{H.c.})$$

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

First-principle exact calculation within the Landauer-Büttiker multi-terminal approach

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

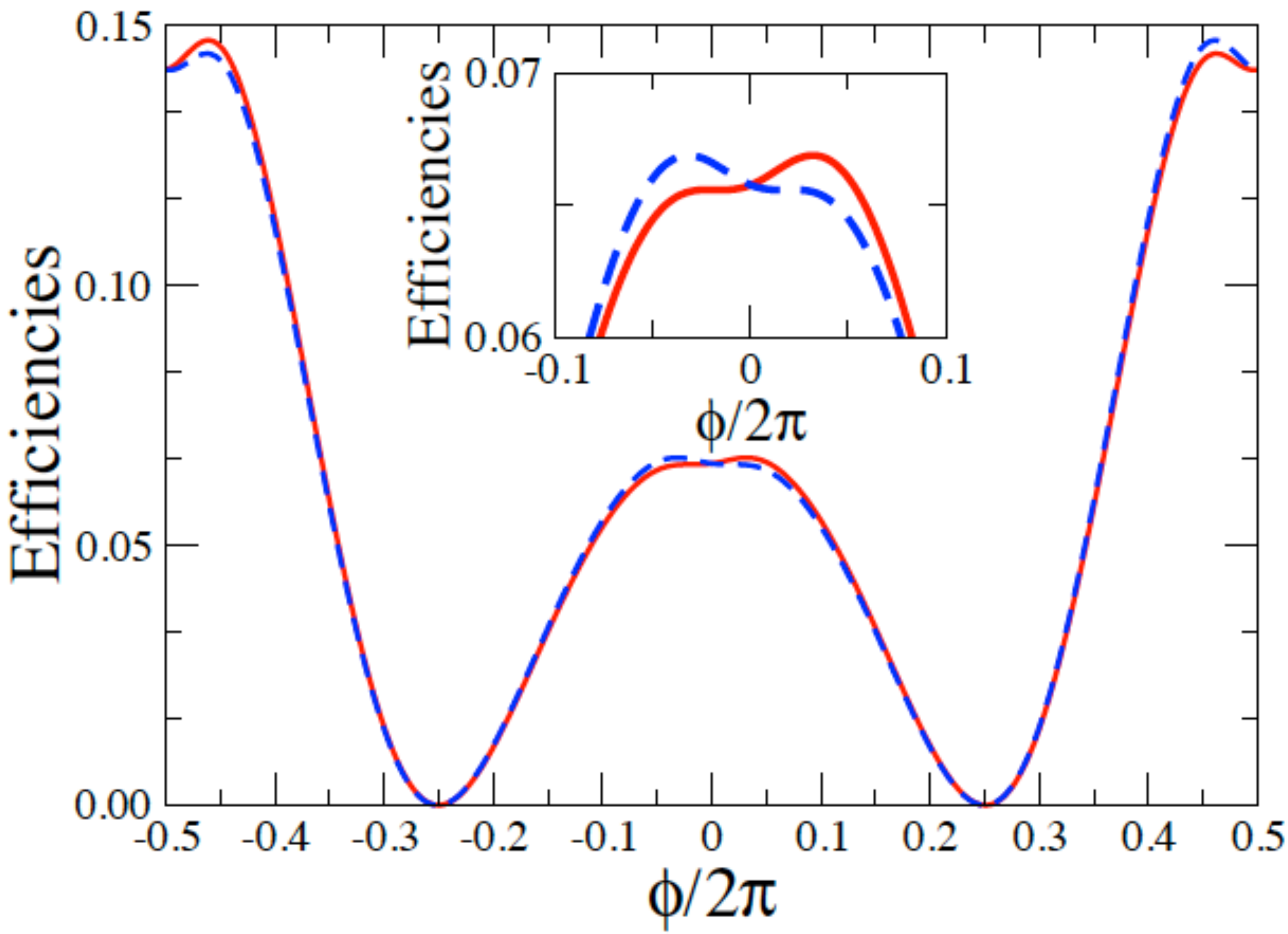
When a magnetic field is added, the efficiencies of power generation and refrigeration are no longer equal:

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

To linear order in the applied magnetic field:

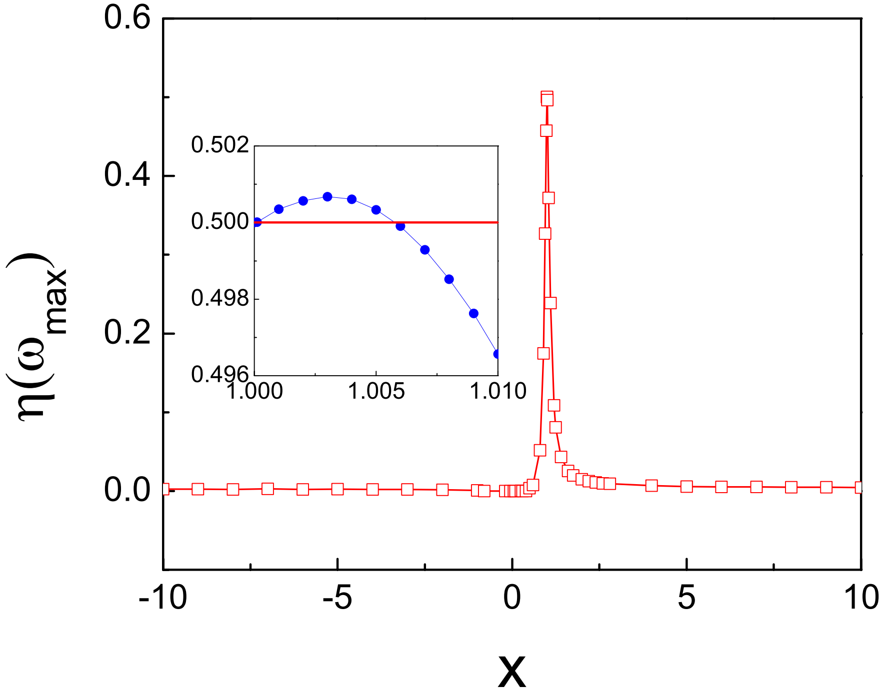
$$\frac{1}{2}\left[\frac{\eta_{\max}(\boldsymbol{B})}{\eta_C} + \frac{\eta_{\max}^{(r)}(\boldsymbol{B})}{\eta_C^{(r)}}\right] = \frac{\eta_{\max}(\mathbf{0})}{\eta_C} = \frac{\eta_{\max}^{(r)}(\mathbf{0})}{\eta_C^{(r)}}$$

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

Optimized efficiency



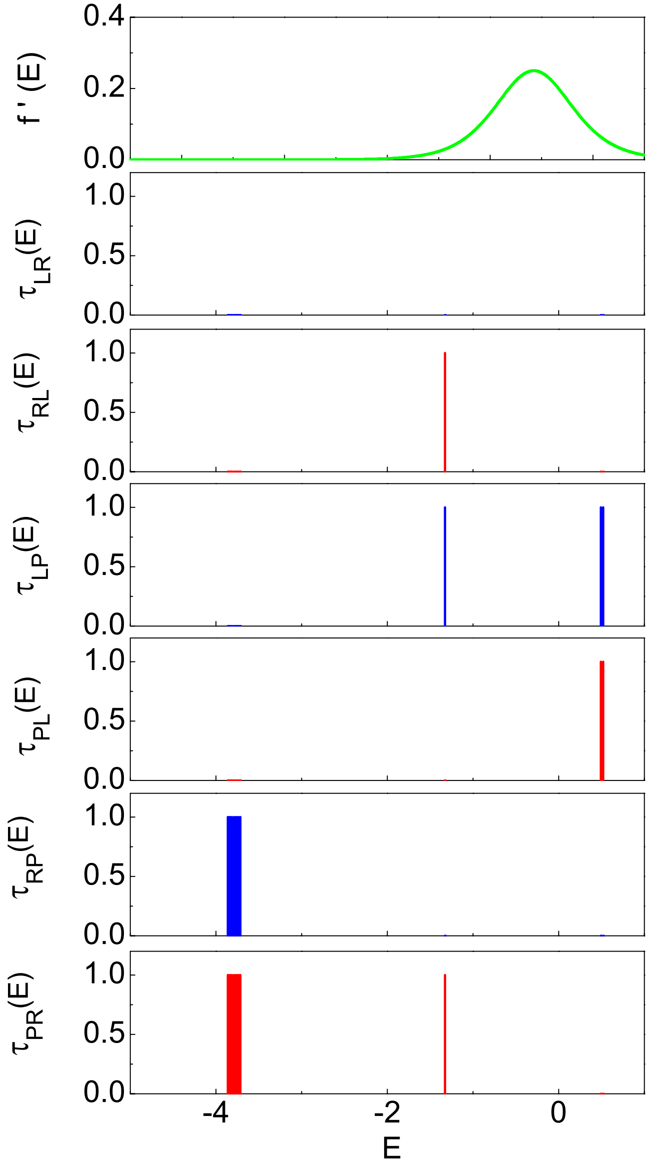
Optimization by means of simulated annealing

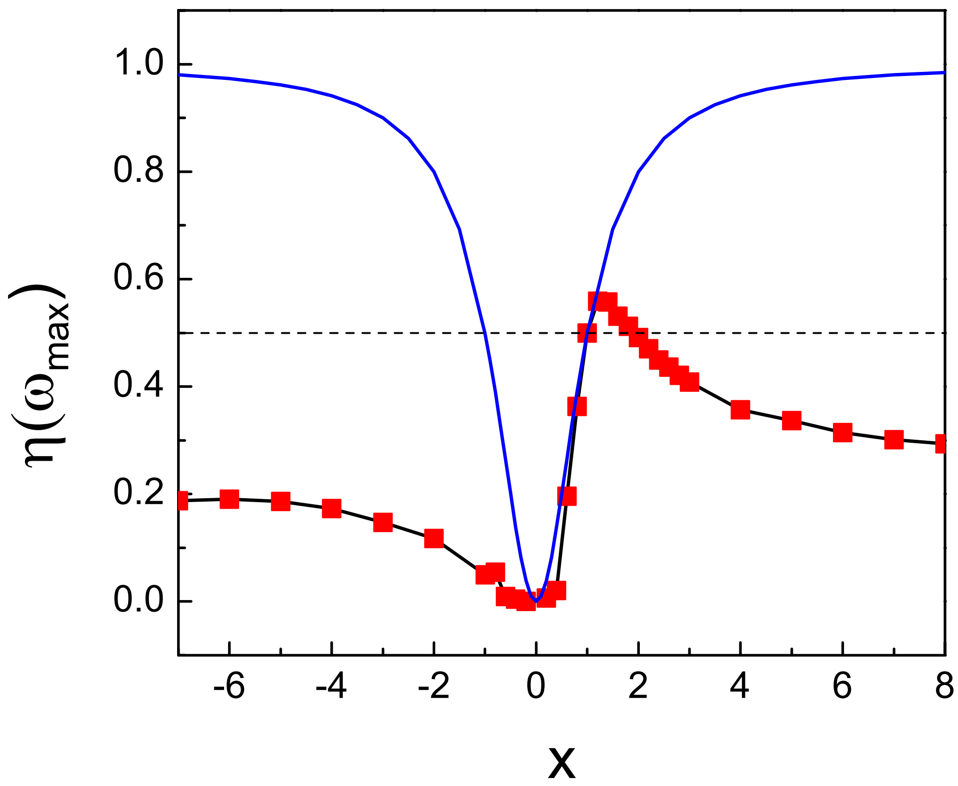
The Curzon-Ahlborn limit can be overcome (within linear response)

(V. Balachandran, G. B., G. Casati, PRB **87**, 165419 (2013))

Transmission windows model

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



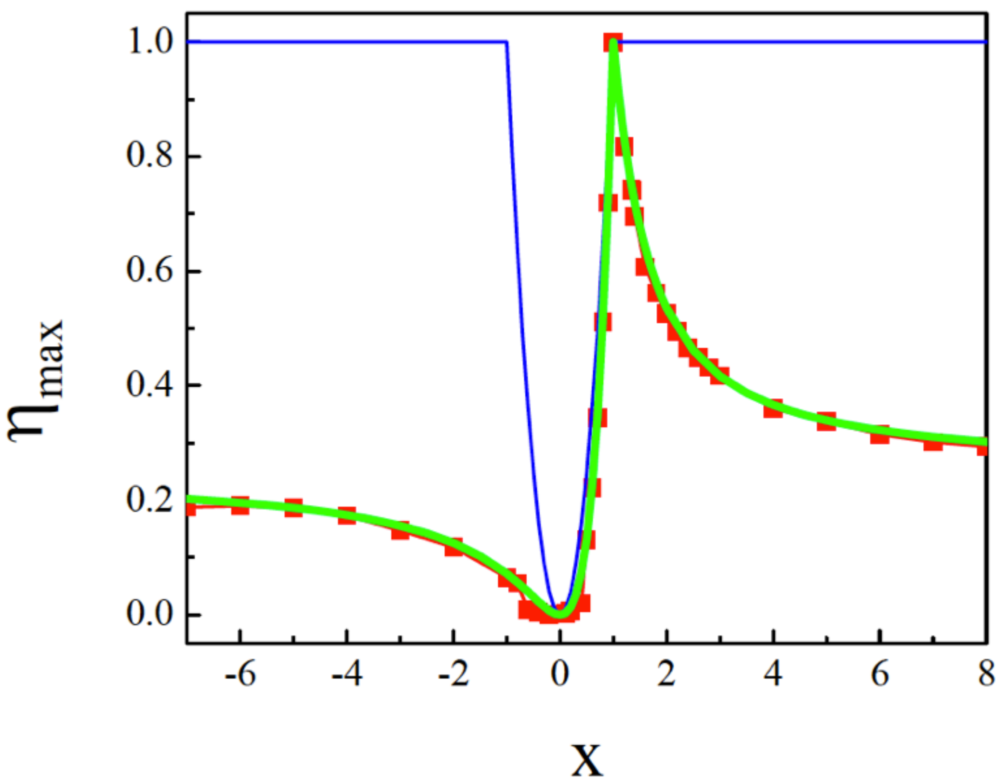


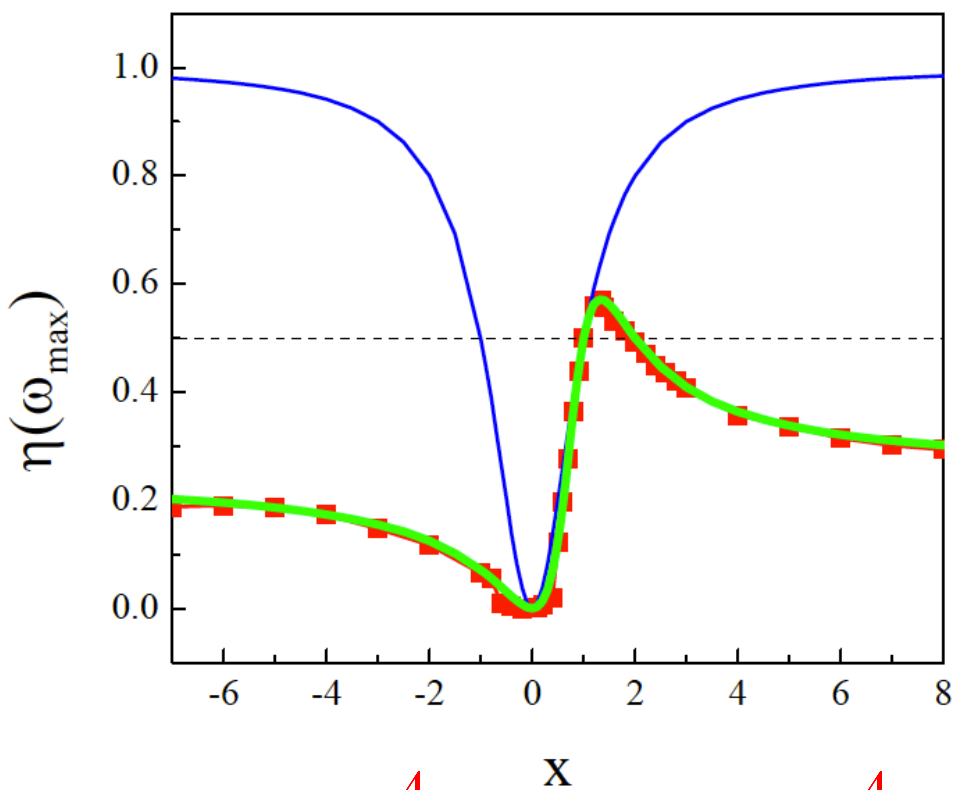
(V. Balachandran, G. B., G. Casati, PRB **87**, 165419 (2013));
se also M. Horvat, T. Prosen, G. B., G. Casati, PRE **86**, 052102 (2012))

Saturation of bounds from the unitarity of S-matrix

Bounds recently obtained for non-interacting 3-terminal transport

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





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

Magnetic thermal switch (n-terminal setup)

$$\mathbf{J}(\mathbf{B}) = \mathbf{J}^{(r)}(\mathbf{B}) + \mathbf{J}^{(i)}(\mathbf{B})$$

$$\mathbf{J}^{(r)} \equiv \frac{\mathbf{L}(\mathbf{B}) - \mathbf{L}^T(\mathbf{B})}{2}\mathbf{X}, \quad \mathbf{J}^{(i)} \equiv \frac{\mathbf{L}(\mathbf{B}) + \mathbf{L}^T(\mathbf{B})}{2}\mathbf{X}$$

$$\mathbf{J}^{(r)}(\mathbf{B}) \;=\; -\mathbf{J}^{(r)}(-\mathbf{B}) \qquad \mathbf{J}^{(i)}(\mathbf{B}) \;=\; \mathbf{J}^{(i)}(-\mathbf{B})$$

Set voltages (for fixed thermal affinities) to obtain conditions on the currents from a subset K of the n terminals:

$$J_k^Q(-\mathbf{B}) = \sum_{k'=1}^{n-1} x_{kk'}^{(\mathrm{target})}\, J_{k'}^Q(\mathbf{B}), \qquad \forall k \in K$$

(R. Bosisio, S. Valentini, F. Mazza, G.B., V. Giovannetti, R. Fazio, F. Taddei, arXiv:1504.01486)

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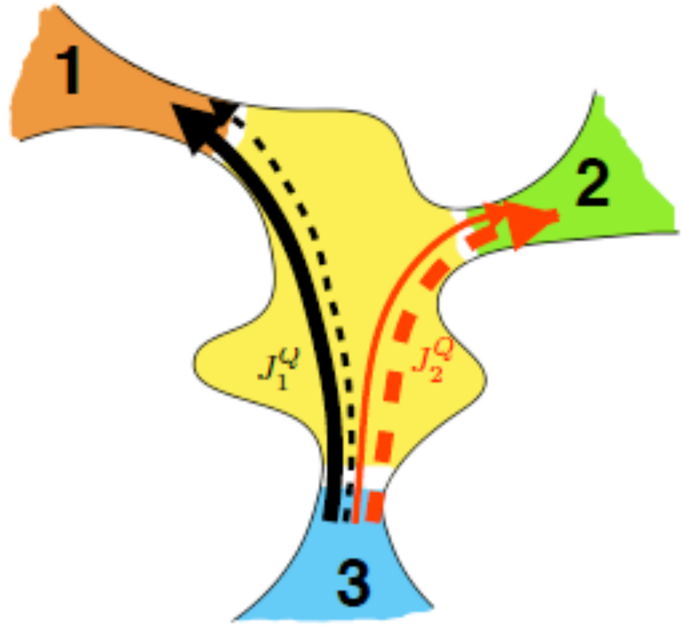
Heat current multiplier:

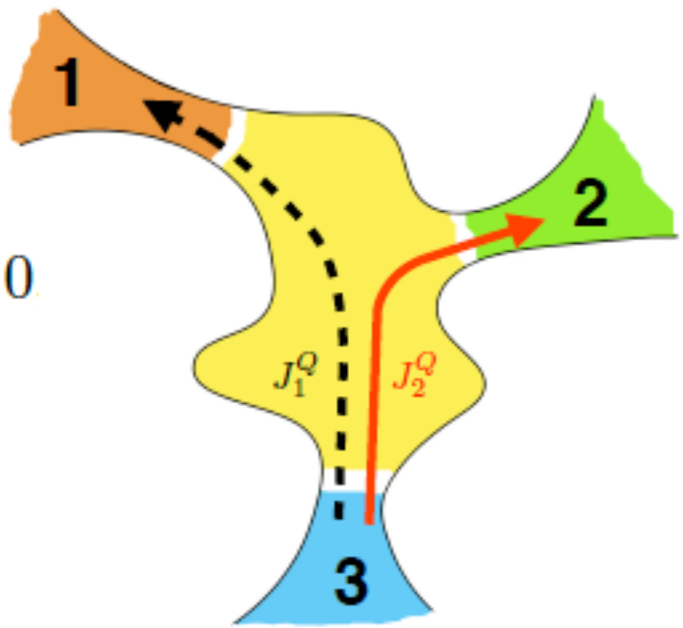
$$J_k^Q(-\mathbf{B}) \;=\; x_k J_k^Q(\mathbf{B})$$



Heat path selector:

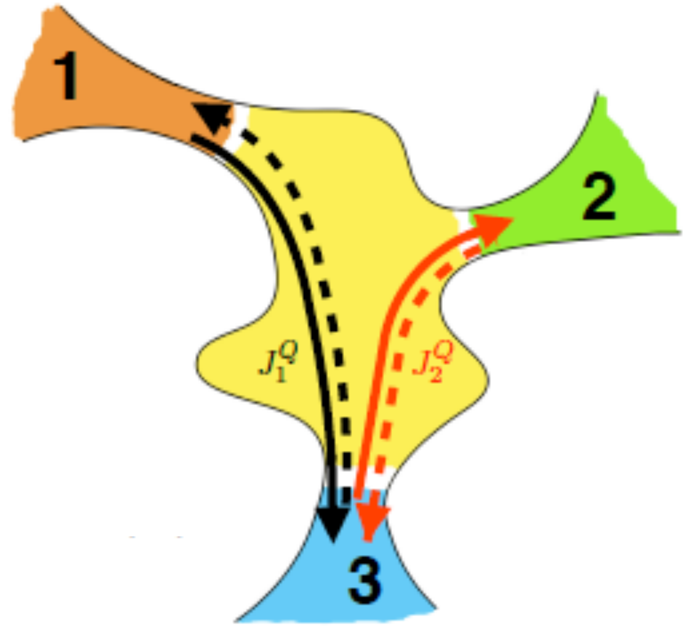
$$J_k^Q(-\mathbf{B}) = J_k^{Q(r)}(-\mathbf{B}) + J_k^{Q(i)}(-\mathbf{B}) = 0$$

$$J_k^Q(\mathbf{B}) = J_k^{Q(r)}(\mathbf{B}) + J_k^{Q(i)}(\mathbf{B}) \neq 0$$



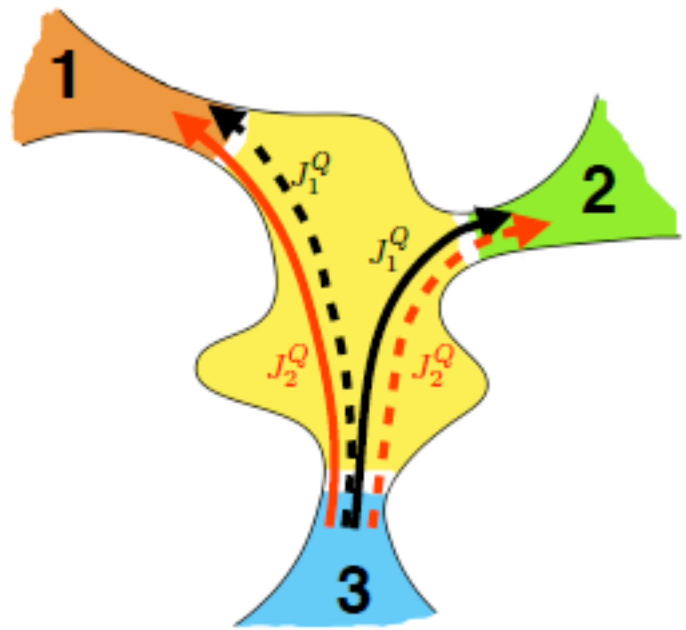
Fully reversible heat:

$$J_k^{Q(i)} = 0$$

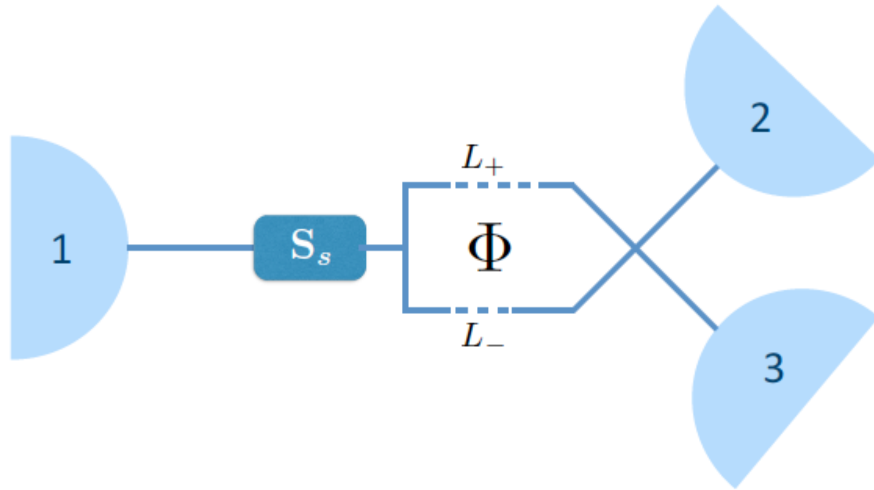


Heat current swap:

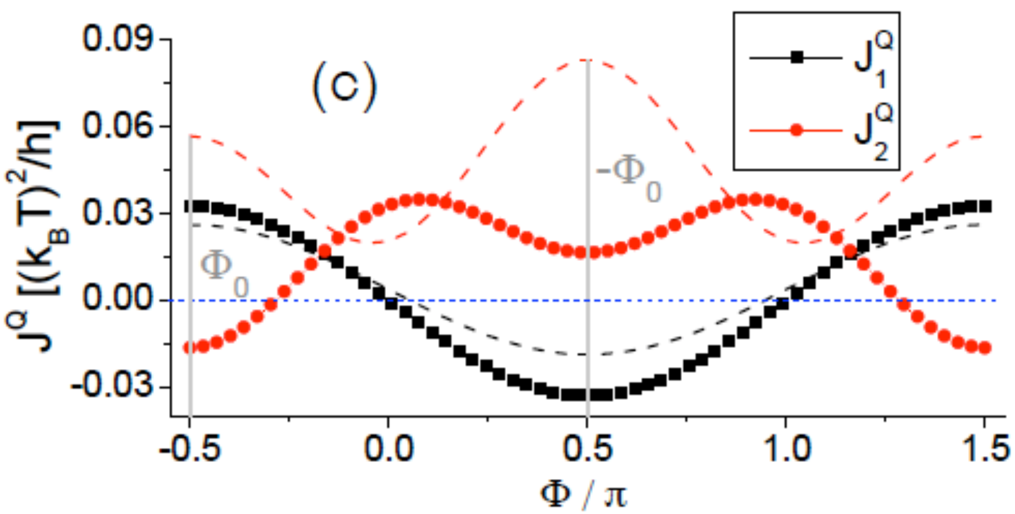
$$J_k^Q(\mathrm{B}) \;=\; J_{k'}^Q(-\mathrm{B})$$
$$J_{k'}^Q(\mathrm{B}) \;=\; J_k^Q(-\mathrm{B})$$



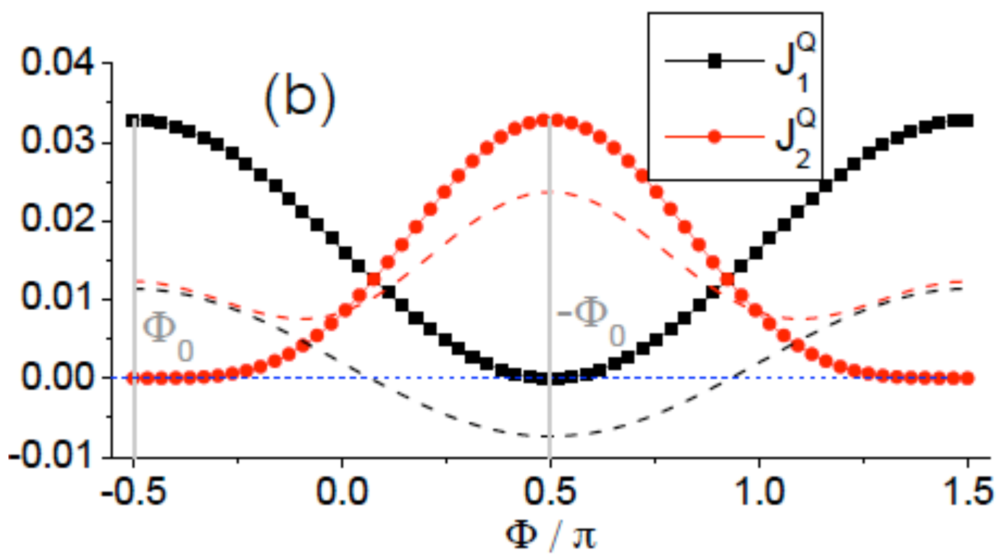
Example: interferometer model



Fully reversible heat:

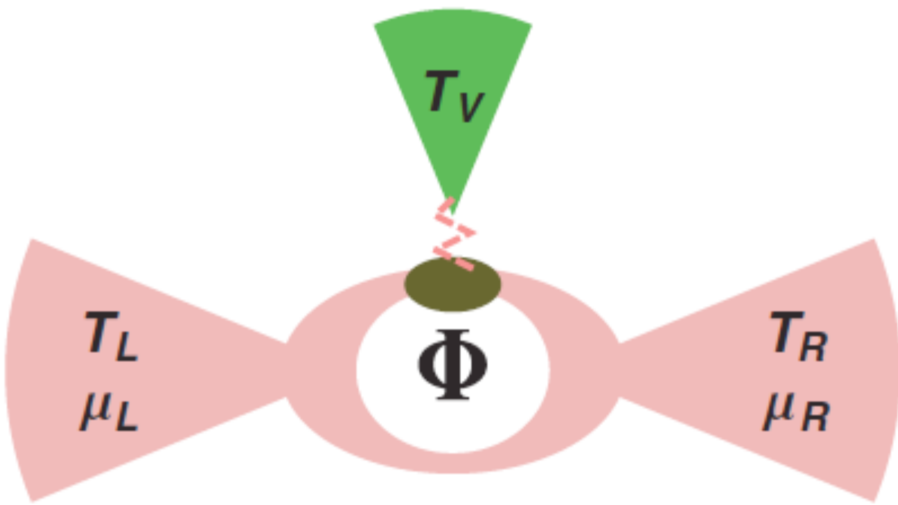


Heat path selector:



(R. Bosisio, S. Valentini, F. Mazza, G.B., V. Giovannetti, R. Fazio, F. Taddei, arXiv:1504.01486)

Switch also applicable to phononic currents



(O. Entin-Wolman, A. Aharony, PRB **85**, 085401 (2012))

Due to electron-phonon coupling the thermal current from the bosonic terminal has a reversible component

Summary

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

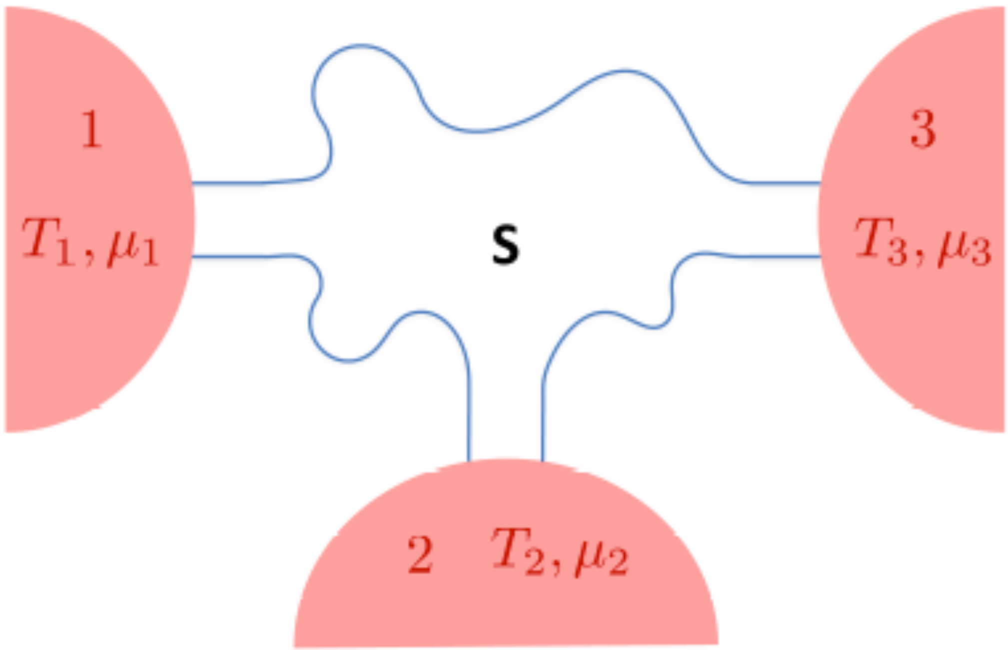
Asymmetric efficiencies of power generation and refrigeration

Magnetic thermal switch for heat management

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-terminalt ransport coefficients

Nonlocal thermopowers

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

Electrical and thermal conductances

$$G_{ij} = \left(\frac{e^2 J_i^N}{\Delta\mu_j}\right)_{\substack{\Delta T_k = 0\ \forall k, \\ \Delta\mu_k = 0\ \forall k \neq j}} \qquad \Xi_{ij} = \left(\frac{J_i^Q}{\Delta T_j}\right)_{\substack{J_k^N = 0\ \forall k, \\ \Delta T_k = 0\ \forall k \neq j}}$$

Peltier coefficients

$$\Pi_{ij} = \left(\frac{J_i^Q}{e J_j^N}\right)_{\substack{\Delta T_k = 0\ \forall k, \\ \Delta\mu_k = 0\ \forall k \neq j}} \qquad \Pi_{ij}(\mathbf{B}) = T S_{ji}(-\mathbf{B})$$

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

Thermoelectric efficiency

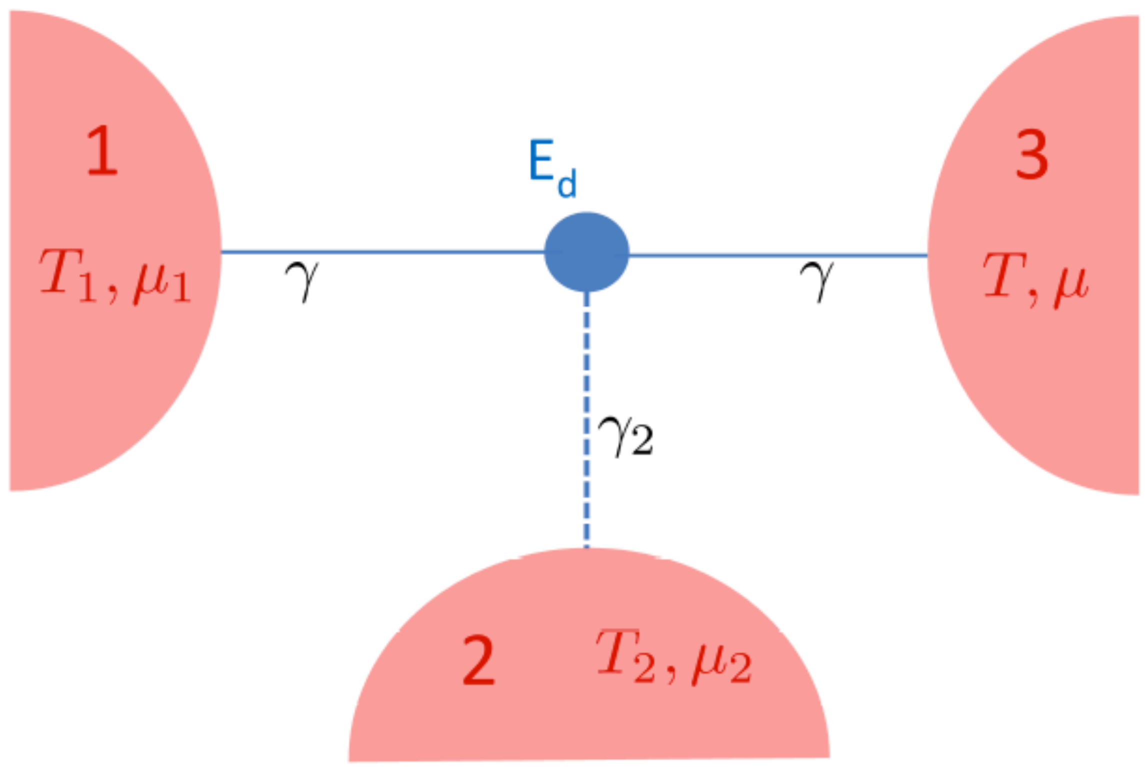
$$\eta = \frac{\dot{W}}{\sum_{i_+} J_i^Q} = \frac{\sum_{i=1}^{3} J_i^Q}{\sum_{i_+} J_i^Q} = \frac{-\sum_{i=1}^{2} \Delta\mu_i J_i^N}{\sum_{i_+} J_i^Q}$$

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

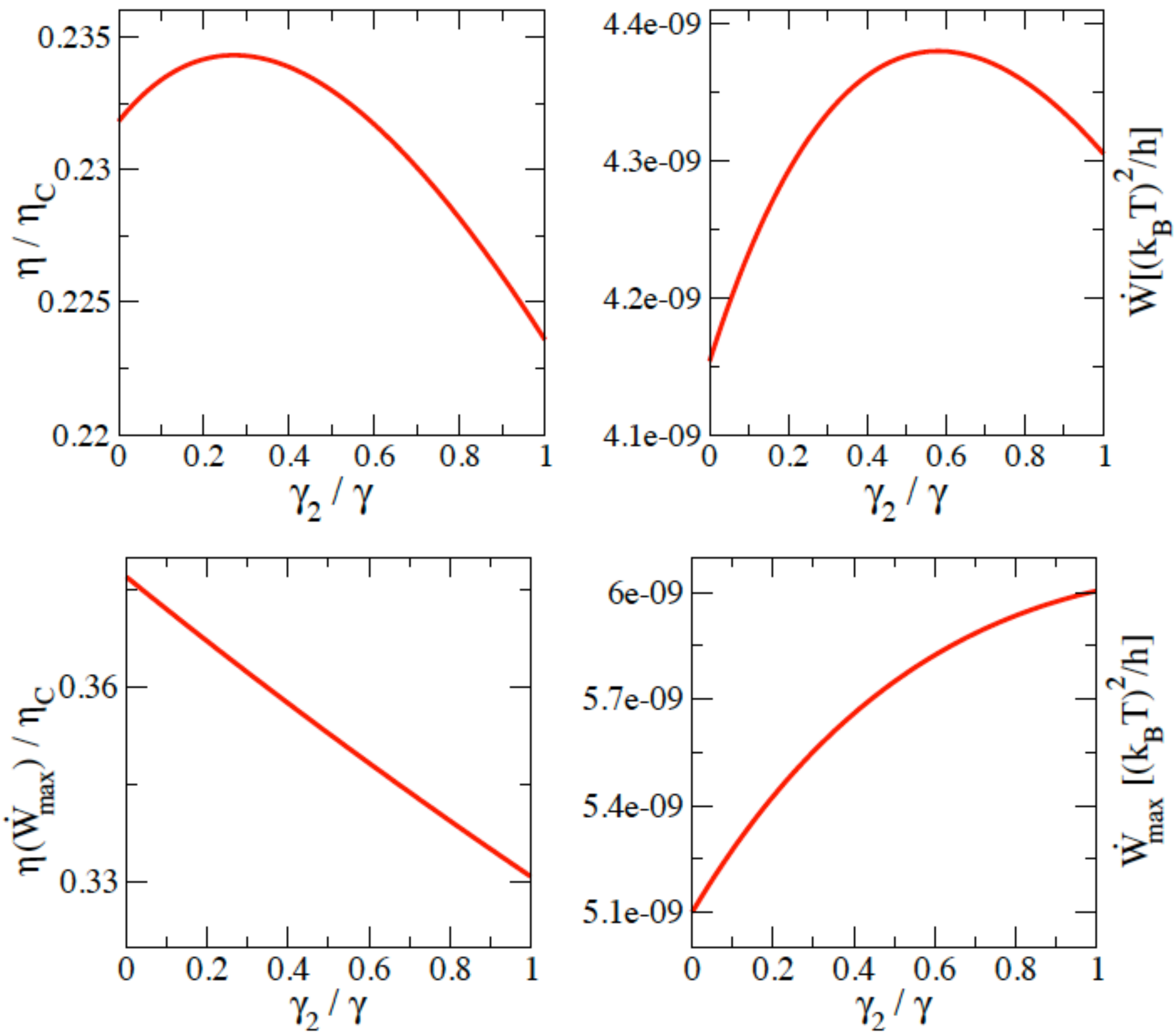
(F. Mazza, R. Bosisio, G. B., V. Giovannetti, R. Fazio, F. Taddei, New J. Phys. **16**, 085001 (2014))

Illustrative example: single dot

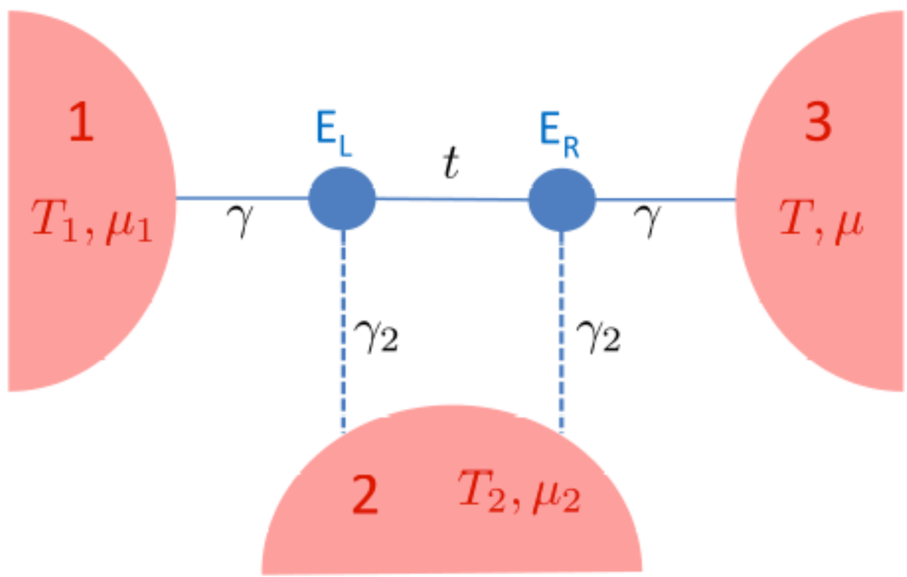


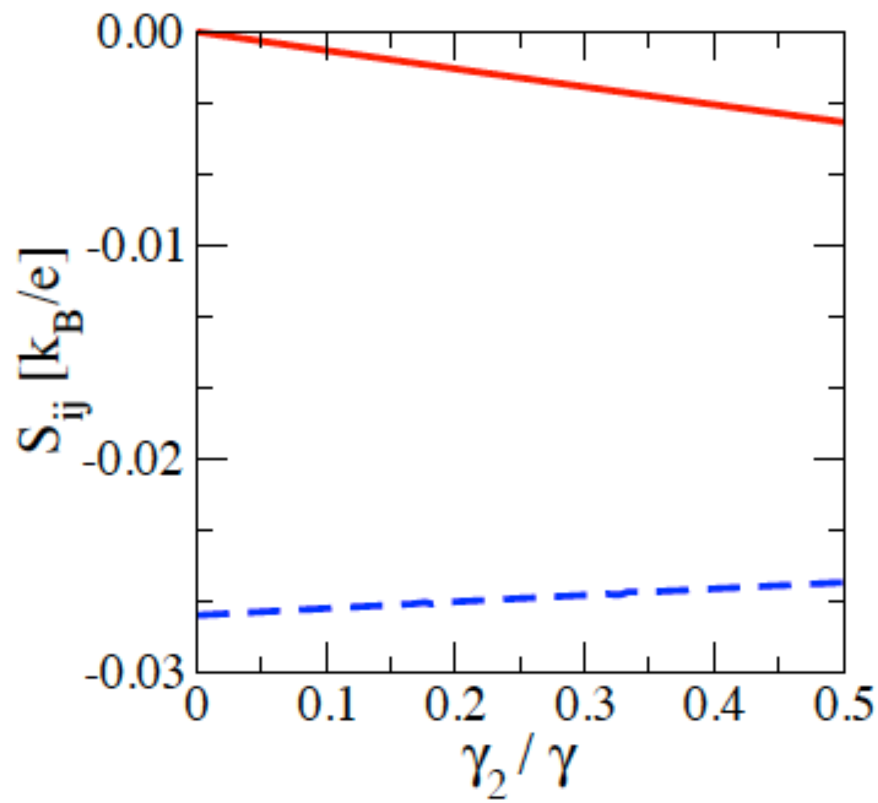
Terminal 2 is at temperature between T_1 and T_3

Improving power and/or efficiency



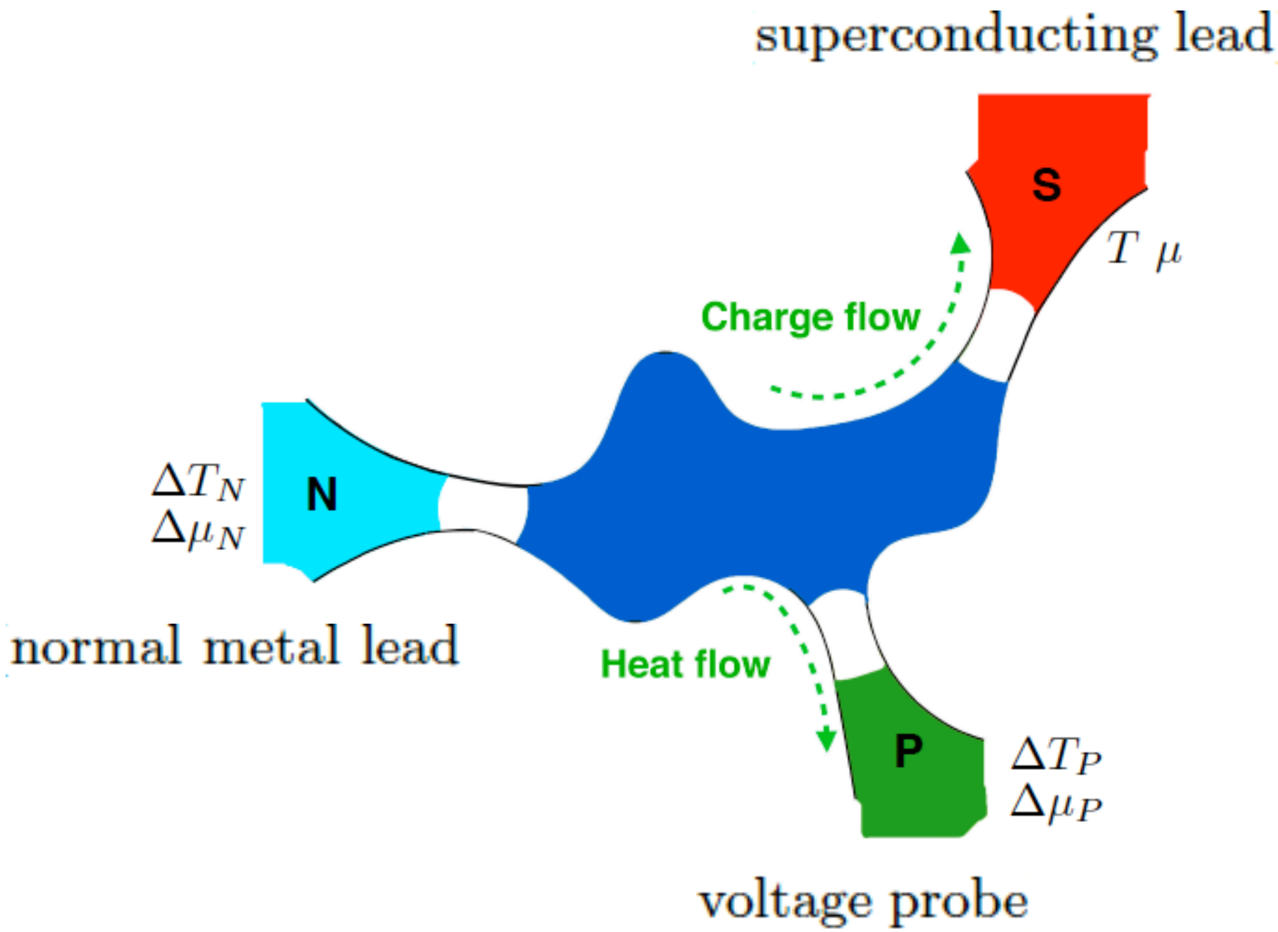
Illustrative example: double dot





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

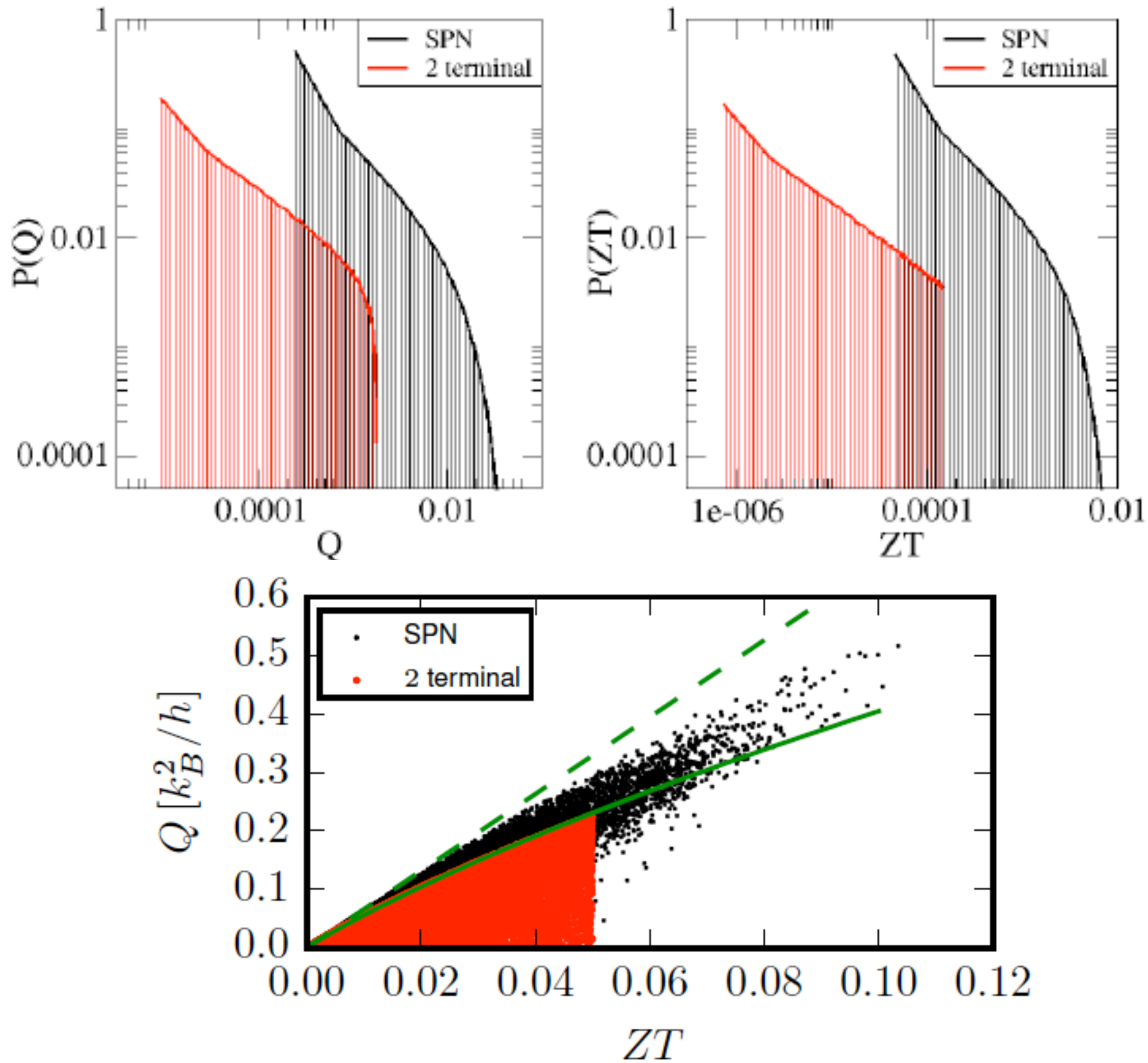
Heat-charge separation



(F. Mazza, S. Valentini, R. Bosisio, G.B., R. Fazio, V. Giovannetti, F. Taddei, arXiv:1503.01601)

Improved thermoelectric performances

Statistics of scattering matrices (within the Sommerfeld regime)



Summary (part III)

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,
- systems with time-dependent driving (microscopic thermodynamic cycles)