Increasing thermoelectric efficiency: Dynamical models unveil microscopic mechanisms

Giuliano Benenti

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

In collaboration with:
Giulio Casati (Como)
Keiji Saito (Tokyo)

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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 mechanisms leading to high thermoelectric efficiency from the study of nonlinear dynamical systems?

A toy model: a 1D diatomic disordered chain of hard-point elastic particles: a new mechanism is needed to justify the numerically observed large ZT values

Part II: Thermoelectric efficiency in systems with time-reversal breaking

Providing a sustainable supply of energy to the world's population will become a major societal problem for the 21st century as fossil fuel supplies decrease and world demand increases.

Thermoelectric phenomena are expected to play an increasingly important role in meeting the energy challenge of the future.

…a newly emerging field of low-dimensional thermoelectricity, enabled by materials nanoscience and nanotechnology.

Dresselhaus et al: ***Adv. Mater. 2007***

Niche applications:

Medical equipments

Radioisotope thermoelectric generators in spacecrafts

Air conditioning in submarines (thermoelectric cooling is quiet)

Thermoelectric-based car seat cooler/heater (Two million car seat cooler/heater sold in 2006- About 2% reduction in fuel consumption)

Key advantages: high reliability, small size, no noise

Use vehicle waste heat to improve fuel economy

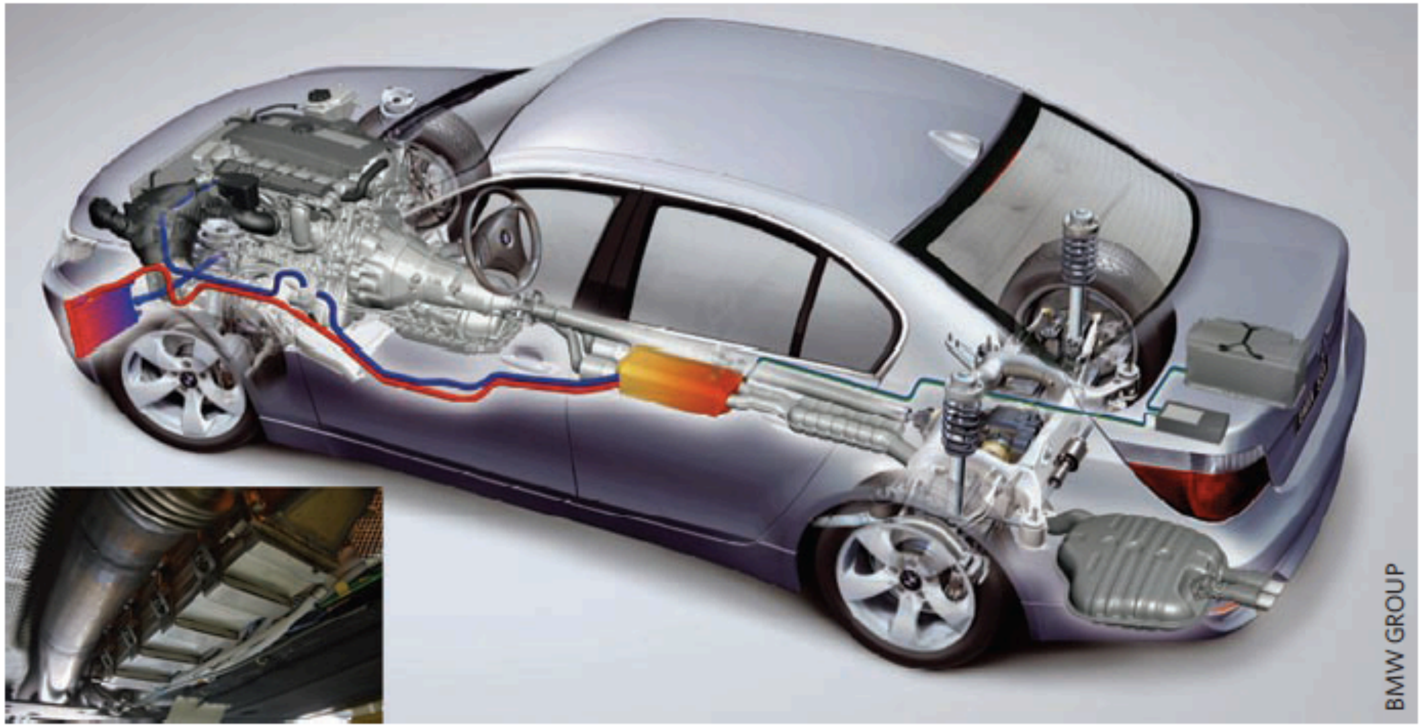
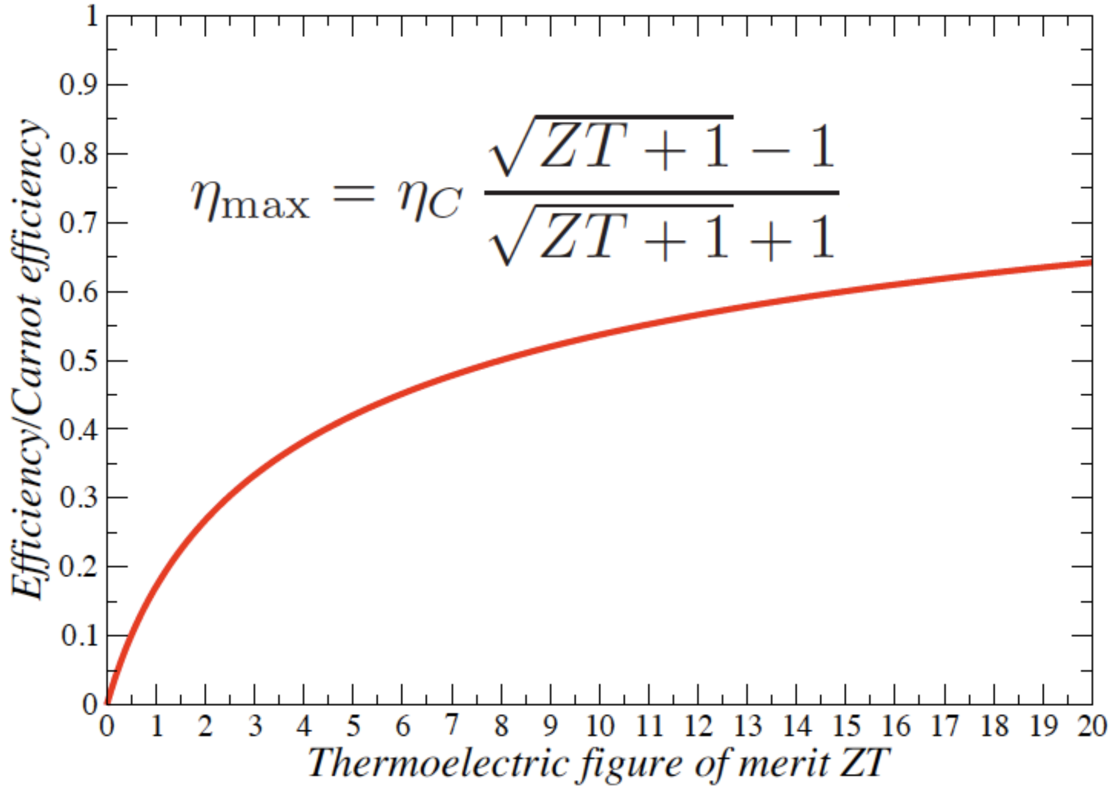


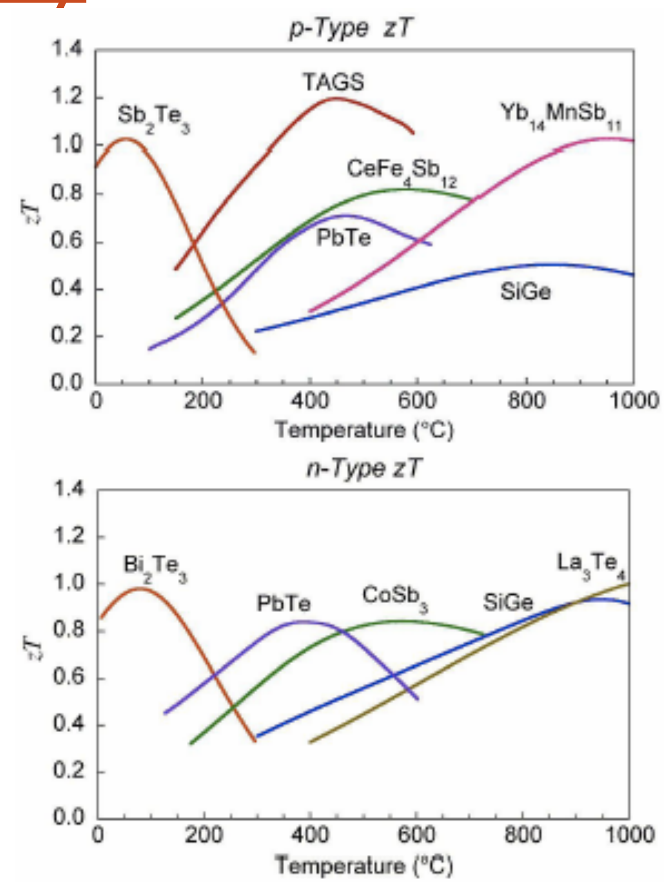
Figure 1 | Integrating thermoelectrics into vehicles for improved fuel efficiency. Shown is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue).

Target: to reach production in the 2011-2014 frame and to improve overall fuel economy by 10%

(see C.B.Vining, Nature Materials **8**, 83 (2009))

Thermoelectric applications are limited due to the low conversion efficiency



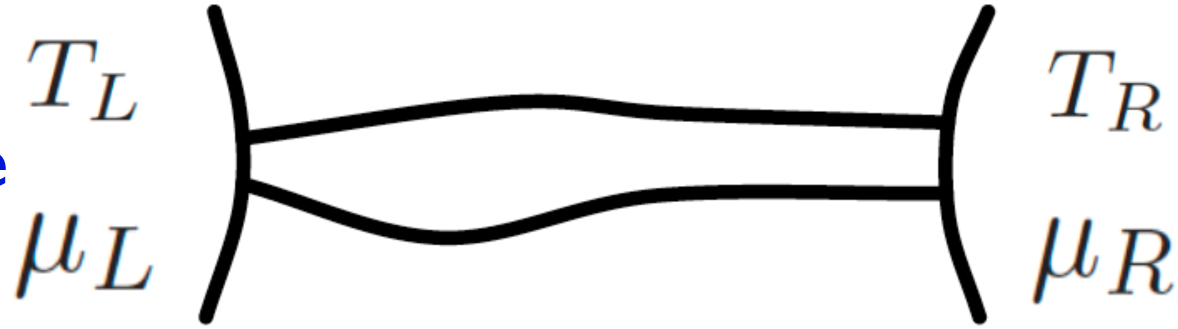


Cronin Vining: *limited role for thermoelectrics in the climate crisis (ZT too small to replace mechanical engines for large-scale applications)*

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 energy transport

Stochastic baths: ideal gases at fixed temperature and chemical potential



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

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

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

$$\beta = 1/T$$

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

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

$$\Delta T = T_R - T_L$$

we assume $T_L > T_R$

Onsager relation:

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

Positivity of entropy production:

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

Onsager and transport coefficients

$$\sigma = \frac{e^2}{T} L_{\rho\rho}, \qquad \kappa = \frac{1}{T^2} \frac{\det \mathbf{L}}{L_{\rho\rho}}, \qquad S = \frac{L_{q\rho}}{eTL_{\rho\rho}}$$

Thermoelectric figure of merit

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

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):

$$J_q \propto J_\rho$$

1D non-interacting classical gas

Particle current

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

$u_\alpha(\epsilon)$ energy distribution of the particles injected from reservoir α

$\mathcal{T}(\epsilon)$ transmission probability for a particle with energy ϵ

$$0 \leq \mathcal{T}(\epsilon) \leq 1$$

Assuming Maxwell-Boltzmann distribution for particles in the baths:

$$u_\alpha(\epsilon) = \beta_\alpha e^{-\beta_\alpha \epsilon}$$

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

(Injection rates)

Particles current:

$$J_\rho = \frac{1}{h} \int_0^\infty d\epsilon \left(e^{-\beta_L(\epsilon-\mu_L)} - e^{-\beta_R(\epsilon-\mu_R)} \right) \mathcal{T}(\epsilon)$$

Heat current:

$$J_{q,\alpha} = \frac{1}{h} \int_0^\infty d\epsilon (\epsilon - \mu_\alpha) \left(e^{-\beta_L(\epsilon-\mu_L)} - e^{-\beta_R(\epsilon-\mu_R)} \right) \mathcal{T}(\epsilon)$$

$$\eta = \frac{J_{q,L} - J_{q,R}}{J_{q,L}}$$

$$= \frac{(\mu_R - \mu_L) \int_0^\infty d\epsilon \left(e^{-\beta_L(\epsilon-\mu_L)} - e^{-\beta_R(\epsilon-\mu_R)}\right) \mathcal{T}(\epsilon)}{\int_0^\infty d\epsilon(\epsilon - \mu_L) \left(e^{-\beta_L(\epsilon-\mu_L)} - e^{-\beta_R(\epsilon-\mu_R)}\right) \mathcal{T}(\epsilon)}$$

If transmission is possible only inside a tiny energy window around $\epsilon = \epsilon_\star$

then $$\eta = \frac{\mu_R - \mu_L}{\epsilon_\star - \mu_L}$$

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

$$\epsilon_\star = \frac{\beta_L \mu_L - \beta_R \mu_R}{\beta_L - \beta_R}$$

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

Carnot efficiency

Delta-like energy-filtering mechanism

[Mahan and Sofo (1996), Humphrey et al. (2002)]

1) Is energy-filtering necessary to get Carnot efficiency?

2) Is strong-coupling necessary?

1) Interacting model with anomalous diffusion

2) Systems without time-reversal symmetry

1D interacting classical gas

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

For $M = m$

$$J_u = T_L \gamma_L - T_R \gamma_R$$

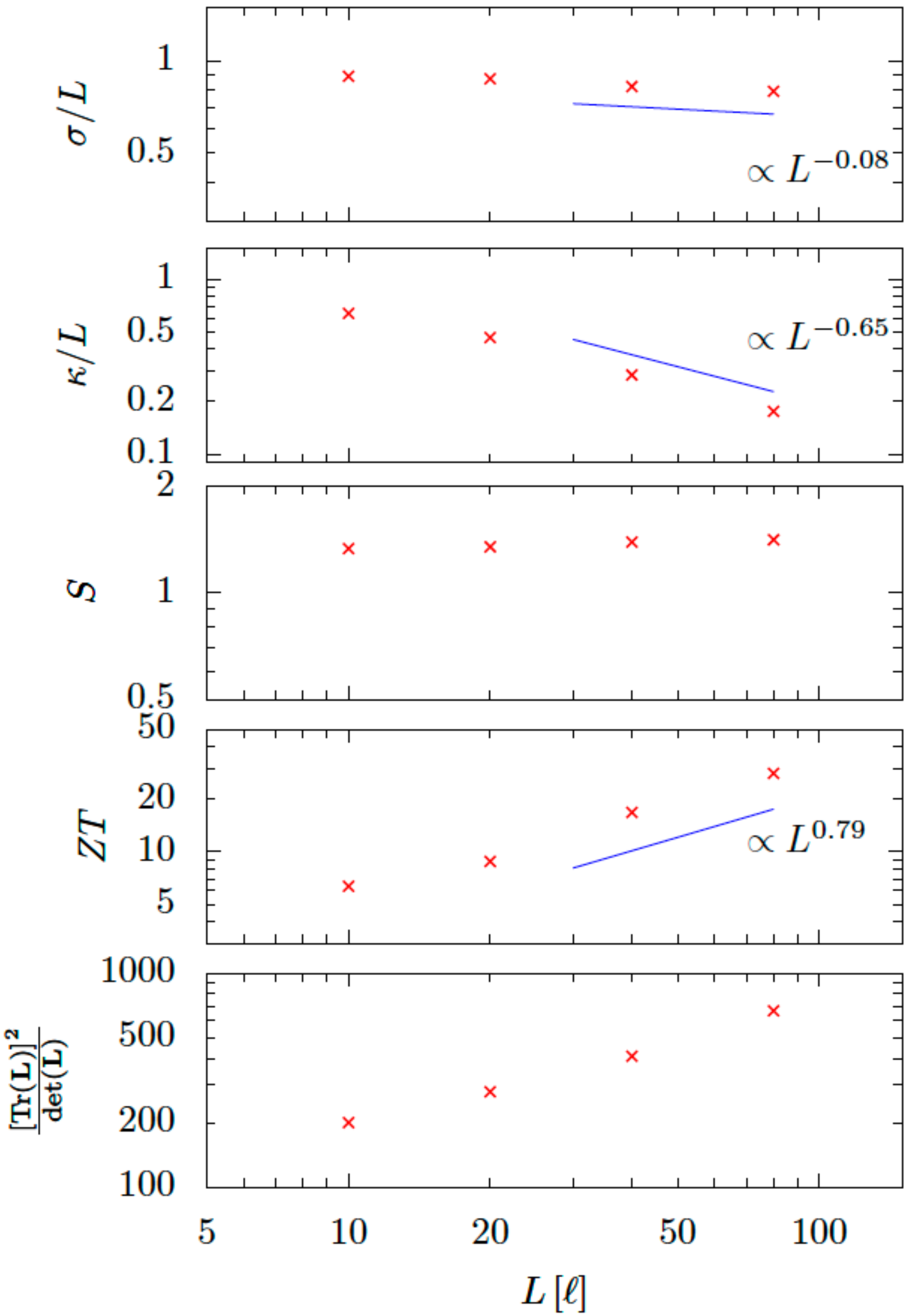
$$J_\rho = \gamma_L - \gamma_R.$$

ZT =1

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

injection rates

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



ANOMALOUS TRANSPORT

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

ZT diverges

increasing the systems size

Energy-filtering mechanism?

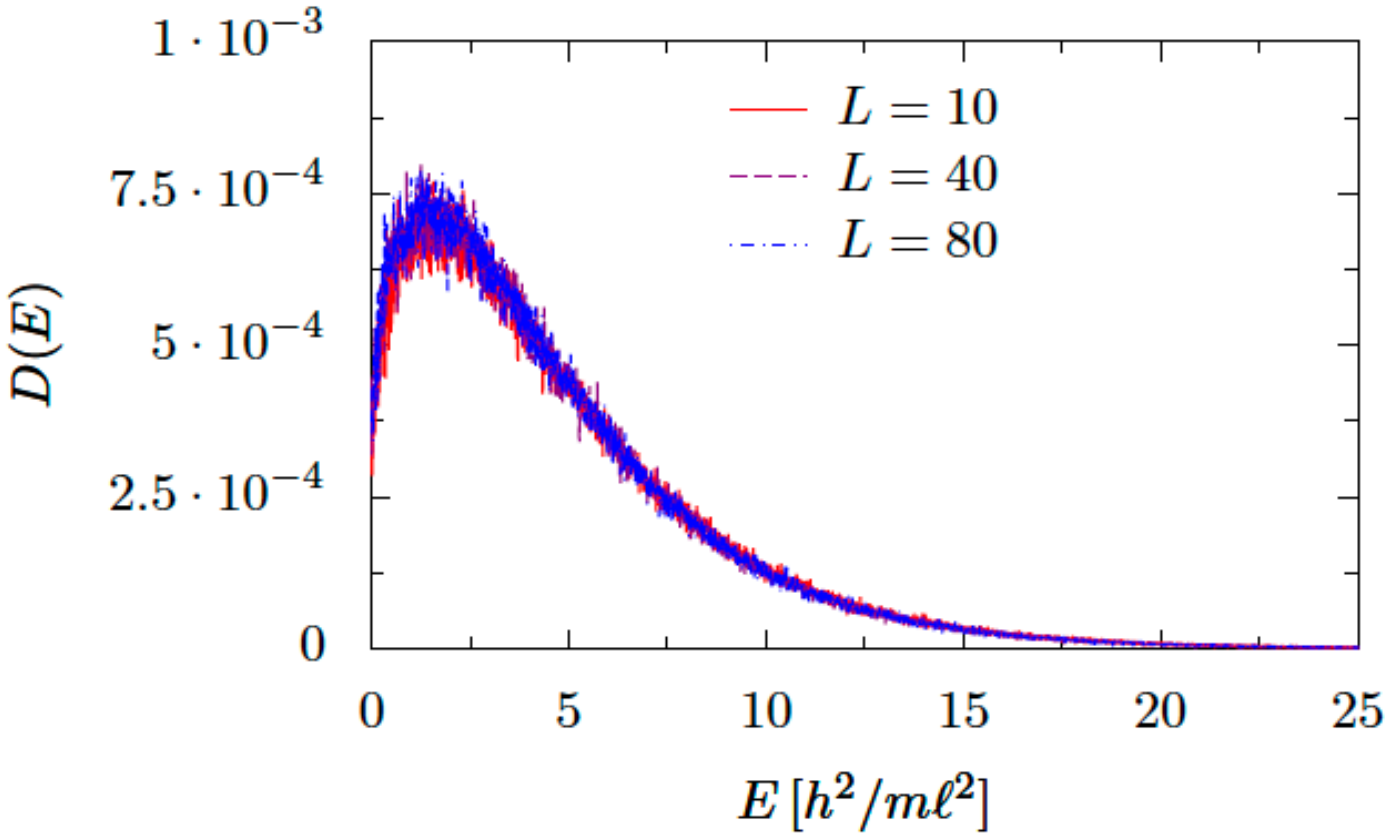
At a given position x compute:

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

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

If the relaxation time scales for density and velocity are well separated:

$$J_\rho = \overline{v(x,t)\rho(x,t)} \quad \sim \overline{v(x,t)} \times \overline{\rho(x,t)}$$

$$J_u = \overline{\frac{1}{2} m v(x,t)^3 \rho(x,t)} \sim \overline{\frac{1}{2} m v(x,t)^3} \times \overline{\rho(x,t)}$$

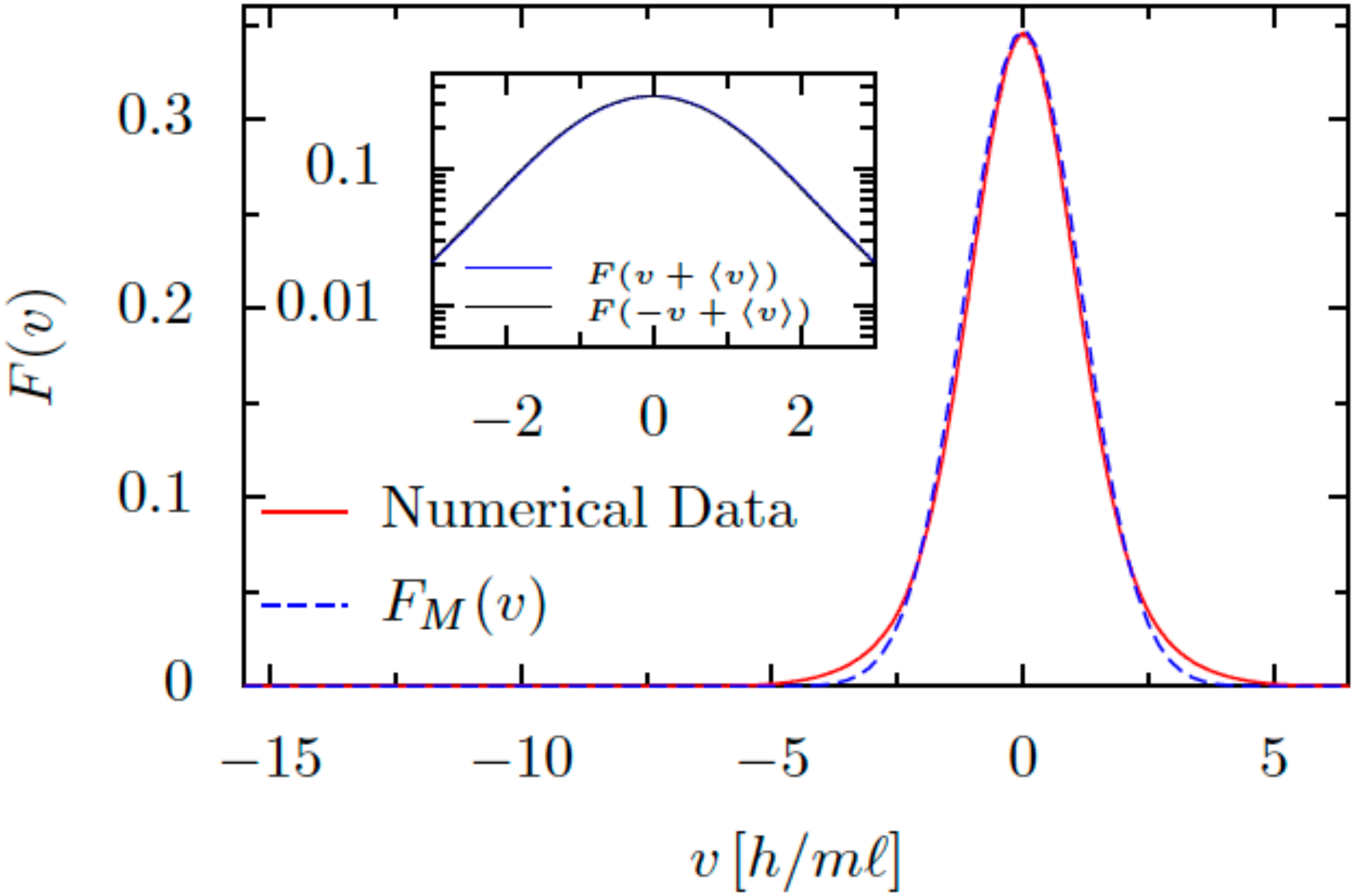
ZT diverges when $J_u \propto J_\rho \quad (J_u = J_q + \mu J_\rho)$

$$\Rightarrow \quad \overline{v^3} \propto \overline{v}$$

Assume time averages $\overline{v^n}$ equal ensemble averages

$$\langle v^n \rangle \equiv \int_{-\infty}^{+\infty} dv v^n F(v)$$

Out of equilibrium Maxwell-Boltzmann distribution



Mean velocity

$\langle v \rangle = 0.010[h/m\ell]$

Width

$\nu = 1.15[h/m\ell]$

$$F_M(v) = \sqrt{\frac{m^\star}{2\pi k_B T}} \exp\left(-\frac{m^\star (v - \langle v \rangle)^2}{2 k_B T}\right)$$

the mean velocity $\langle v \rangle$ and the effective mass $m^\star$ are fitting parameters

From the "out of equilibrium Maxwell-Boltzmann" distribution we obtain

$$\langle v^3 \rangle = \langle v \rangle^3 + 3\nu^2 \langle v \rangle, \qquad \nu \equiv \sqrt{\frac{k_B T}{m^\star}}$$

$$\langle v^3 \rangle \propto \langle v \rangle \text{ when } \nu \gg \langle v \rangle$$

which is verified in our case

Broad velocity distribution of particles across the sample

Summary (part I)

Numerical evidence of the divergence of the thermoelectric figure of merit in a prototype model of interacting 1D gas

Results cannot be explained by the
energy filtering mechanism

Emergence of a broad out-of-equilibrium velocity distribution

The mechanism require:
1) local equilibrium
2) separation of relaxation time scales
3) “out of equilibrium Maxwell-Boltzmann distribution”

Relations with anomalous transport?

Thermoelectric Efficiency for Systems without Time-Reversal Symmetry

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

MAXIMUM EFFICIENCY

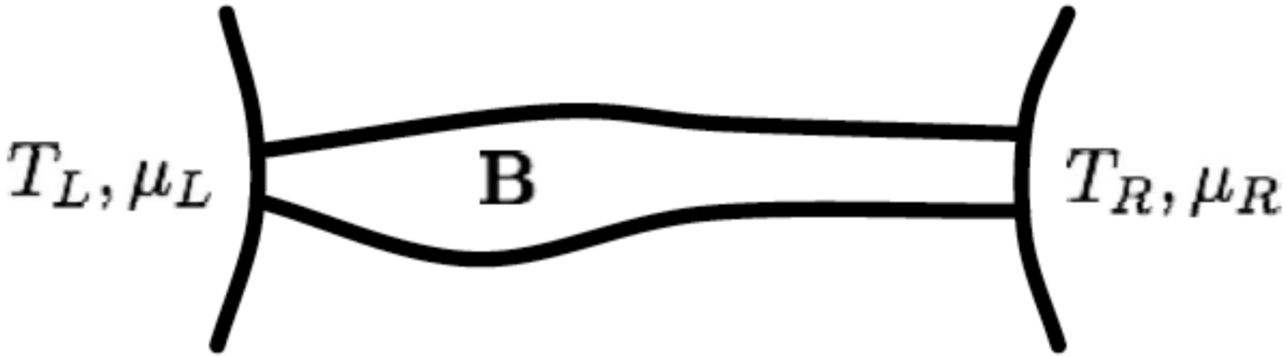
$$\eta_C \frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+1}$$

EFFICIENCY AT MAXIMUM POWER

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

[Van den Broeck, 2005]

And when time-reversal is broken?



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

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

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

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

$$\beta = 1/T$$

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

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

$$\Delta T = T_R - T_L$$

we assume $T_L > T_R$

Constraints from thermodynamics

POSITIVITY OF THE ENTROPY PRODUCTION:

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

ONSAGER-CASIMIR RELATIONS:

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

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

EFFICIENCY AT MAXIMUM POWER

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

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

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

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

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

Efficiency at maximum power depends on <u>two</u> parameters

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

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

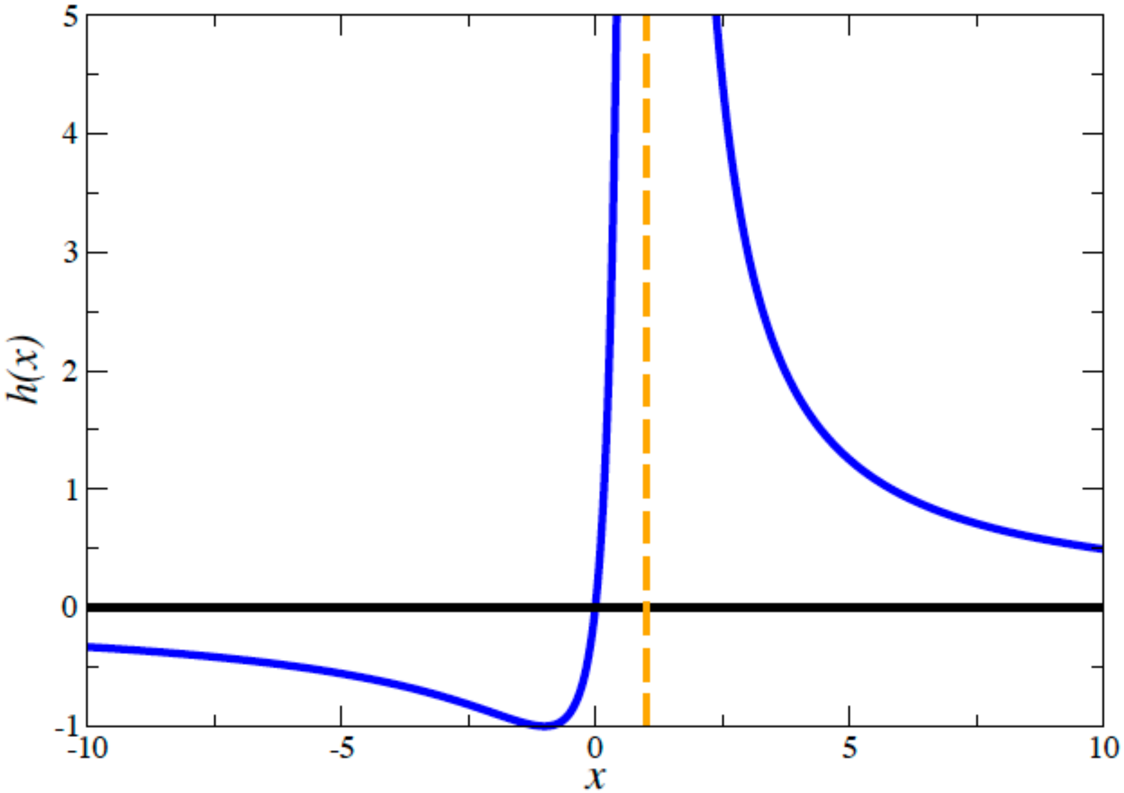
$$\eta(\omega_{\mathrm{max}}) = \frac{\eta_C}{2} \frac{xy}{2+y}$$

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

asymmetry parameter $x = 1$

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

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



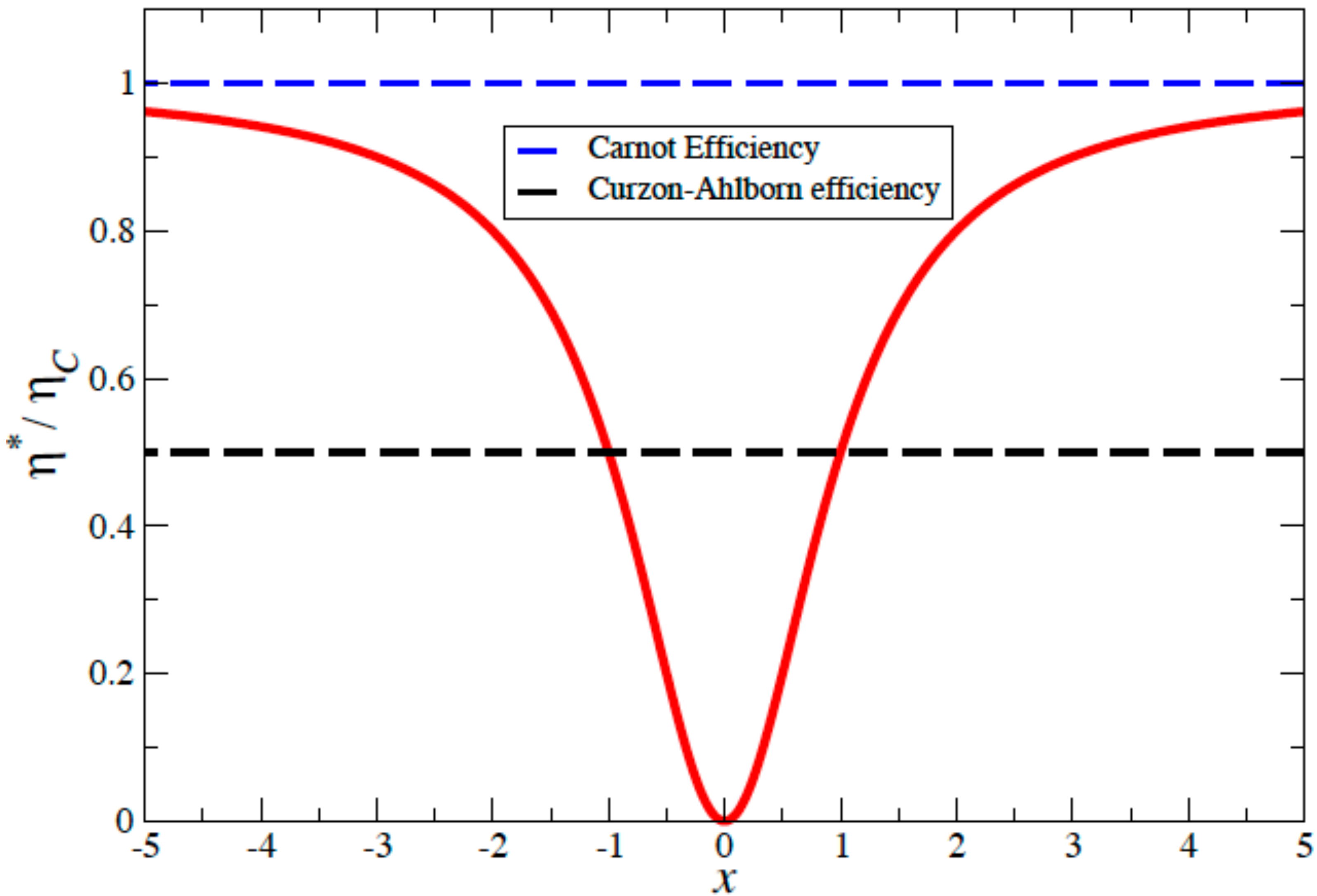
$$h(x) = 4x/(x-1)^2$$

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

achieved for $y = h(x)$

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

The Curzon-Ahlborn limit can be overcome within linear response



MAXIMUM EFFICIENCY

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

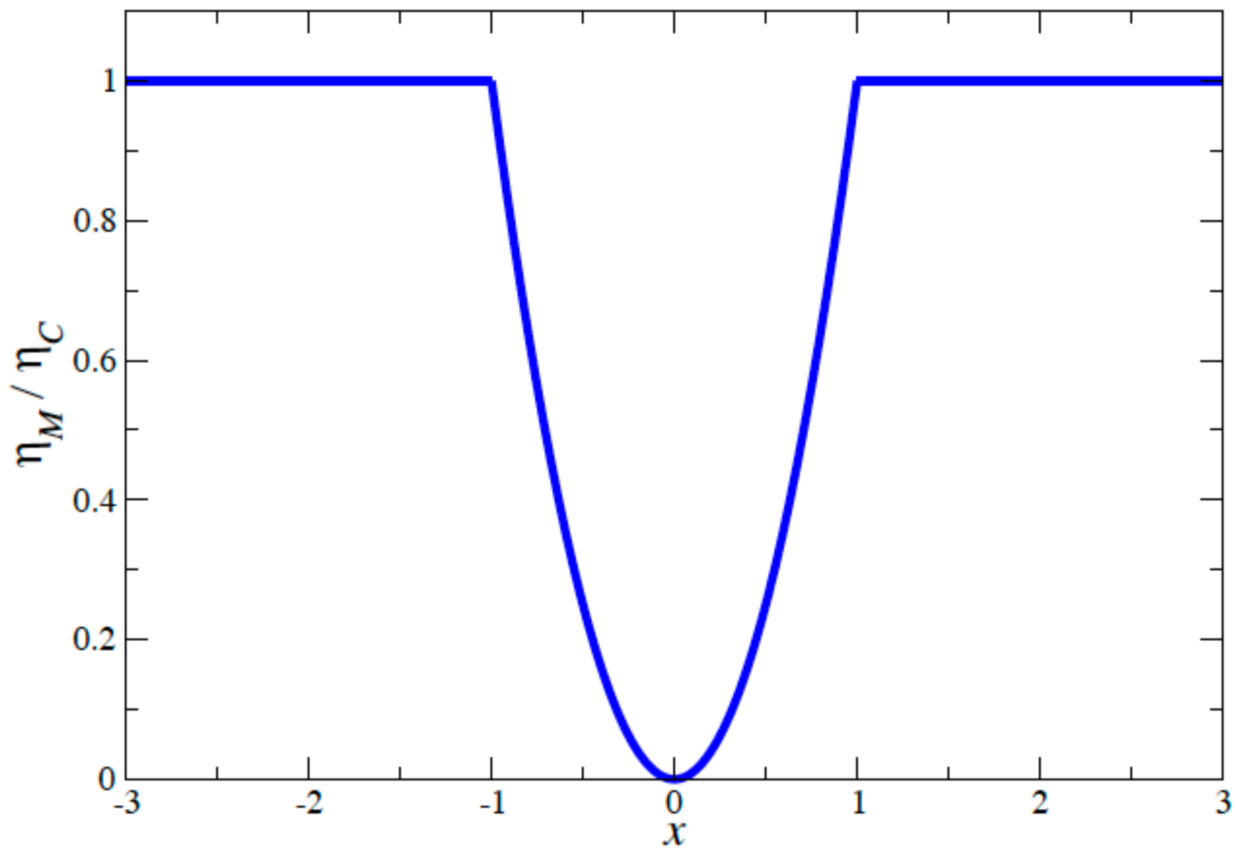
Maximum efficiency achieved for

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

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

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

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



The Carnot limit can be achieved only when

$$|x| \ge 1$$

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

Entropy production rate at maximum efficiency

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

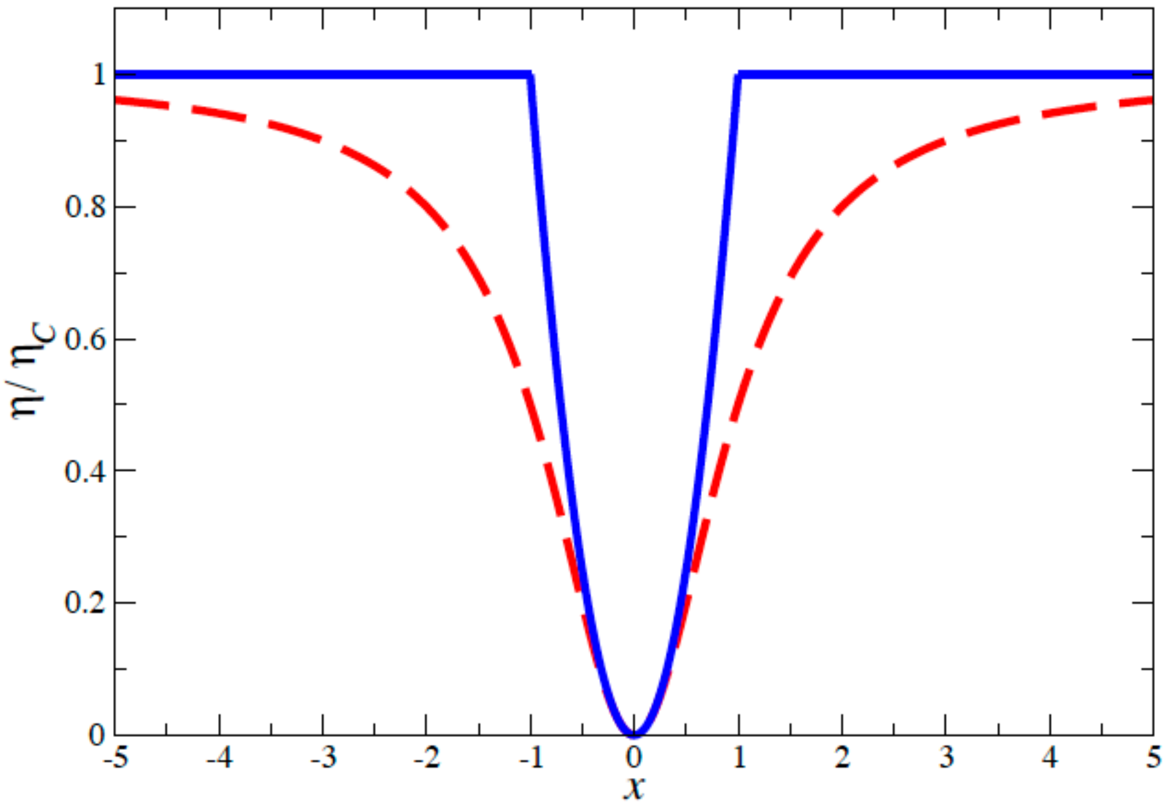
There is no entropy production at |x|>1, in agreement with the fact that in this regime we reach Carnot efficiency

OUTPUT POWER AT MAXIMUM EFFICIENCY

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

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

Terms of higher order in the entropy production will generally be non-zero ➡ shrinking of the validity limits of linear response when approaching Carnot However, we can in principle go closer and closer to the Carnot limit with finite power production



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

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

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

Maximum power at the maximum (Carnot) efficiency

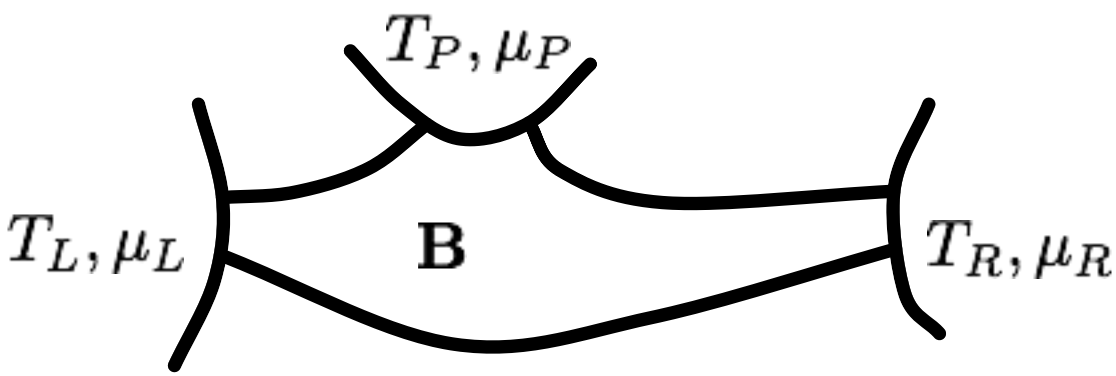
How to obtain asymmetry in the Seebeck coefficient?

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 phase-breaking 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)

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

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

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

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

T_{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:

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

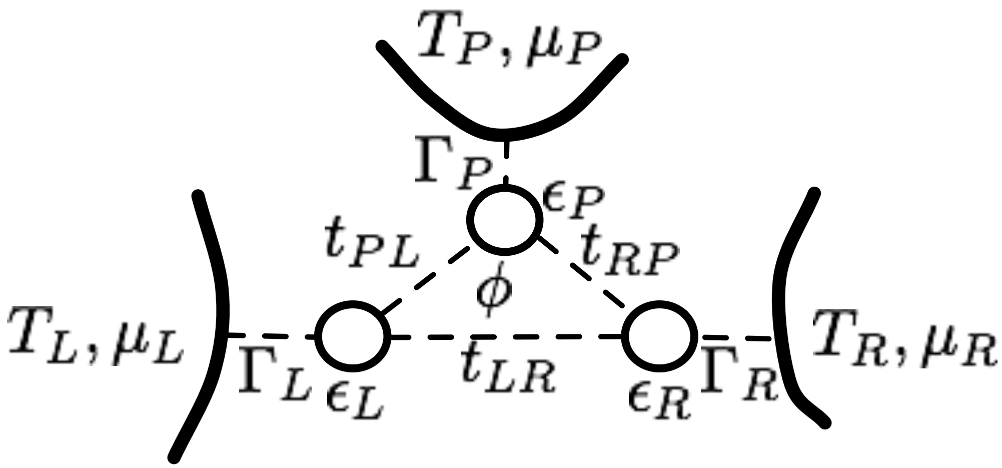
Broadening functions $\Gamma_k(E) \equiv i[\Sigma_k(E) - \Sigma_k^\dagger(E)]$

Self-energies Σ_k

Retarded system's Green function

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

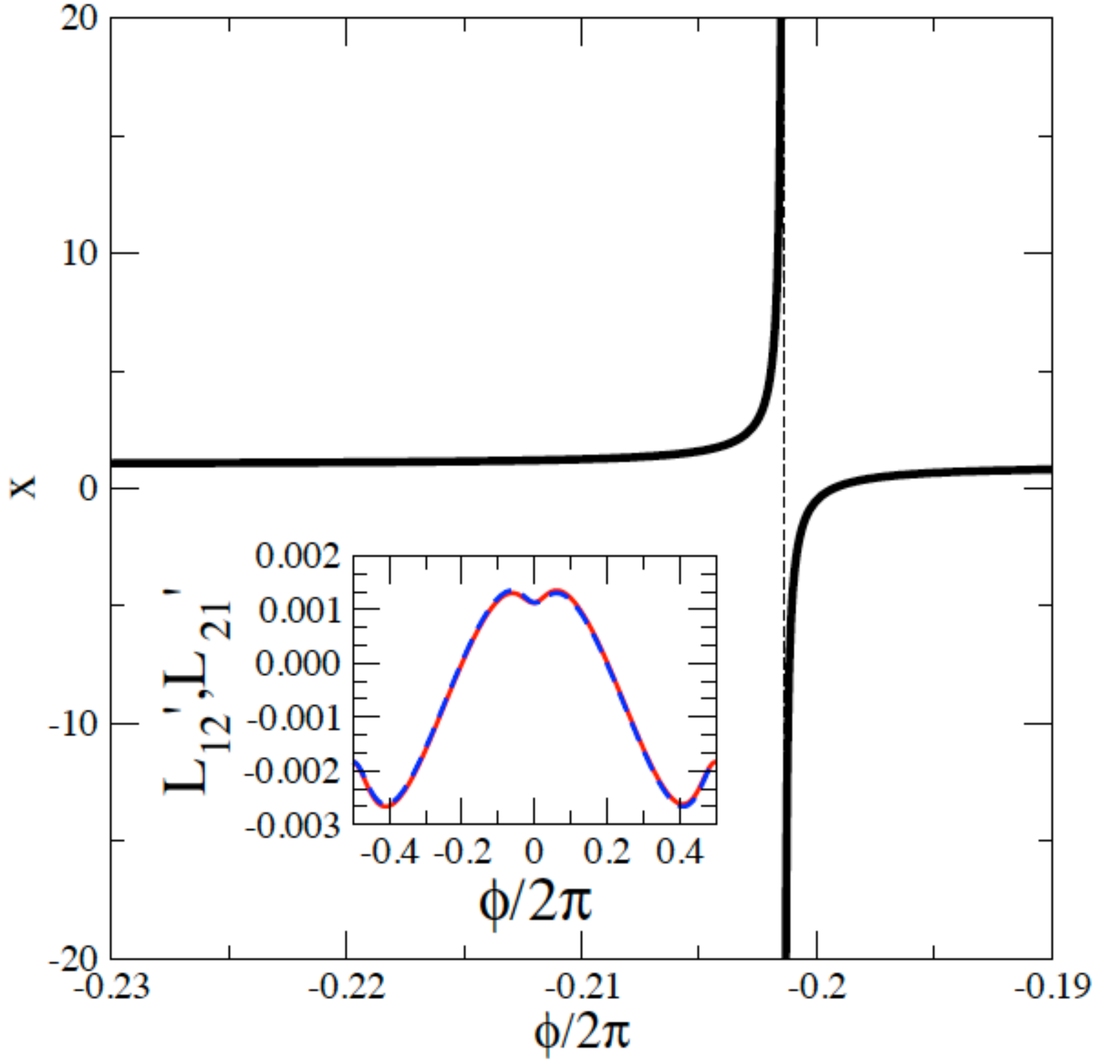
Illustrative three-dot example



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

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

Asymmetric Seebeck coefficient



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

Asymmetric power generation and refrigeration

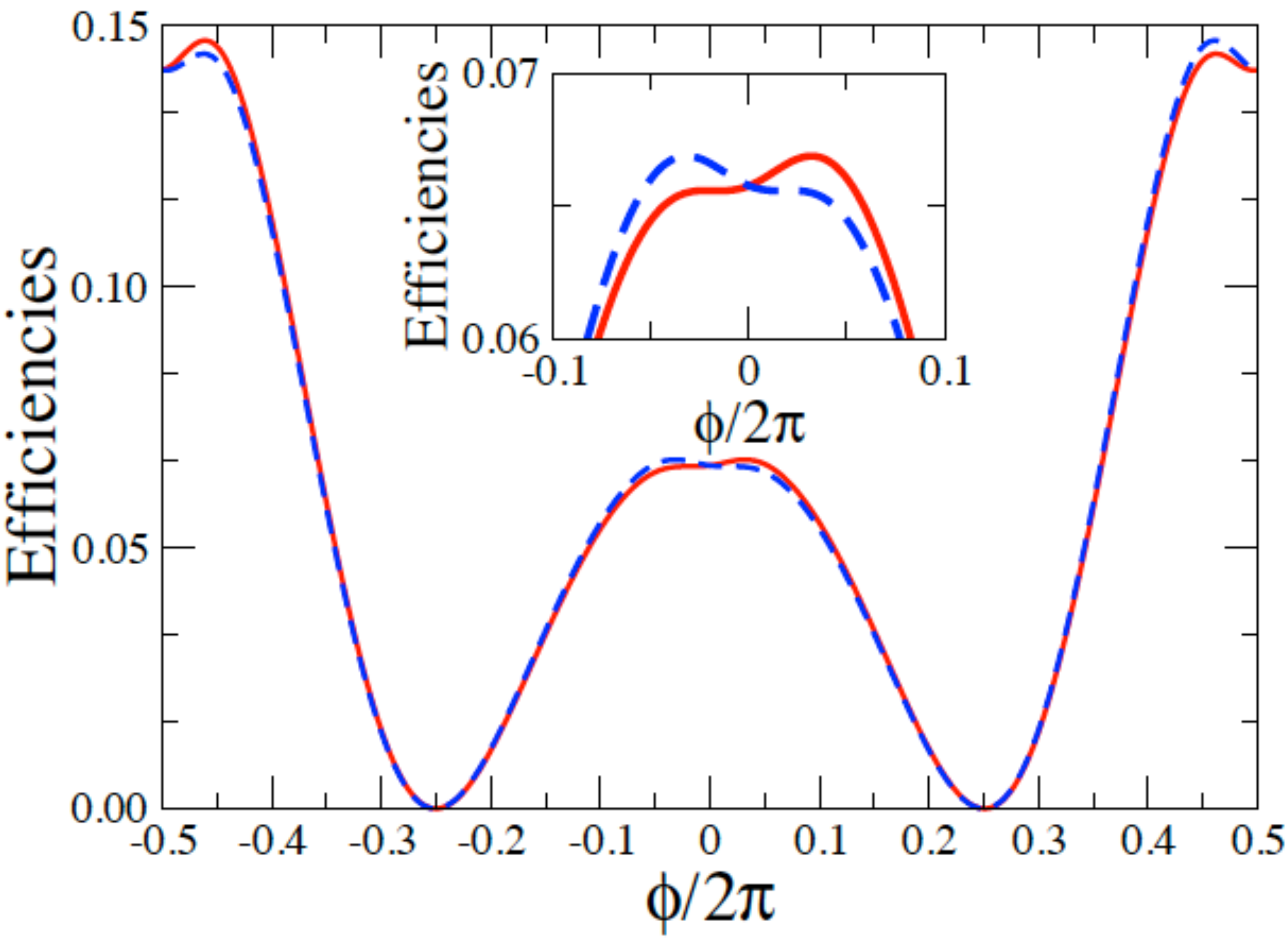
When a magnetic field is added, the efficiencies of power generation and refrigeration are no longer equal:

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

To linear order in the applied flux:

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

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



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

Summary

The Carnot efficiency can be reached without energy filtering (anomalous diffusion in classical hard-point gas)

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

Carnot efficiency in principle achievable far from the strong coupling regime $J_\rho \propto J_q$

The Curzon-Ahlborn limit can be overcome

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