Microscopic Mechanism for Increasing Thermoelectric Efficiency

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OUTLINE

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

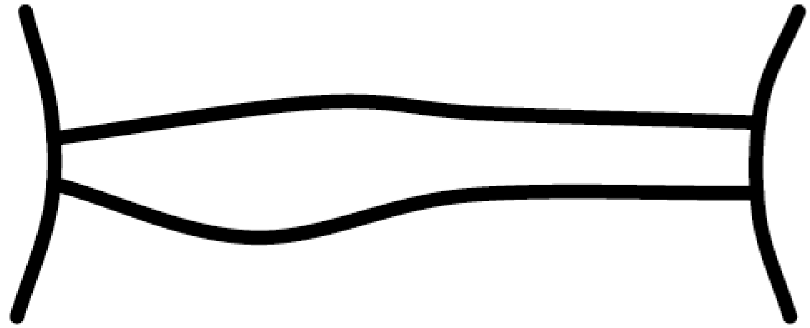
A new mechanism is needed to justify the numerically observed large ZT values

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

Coupled 1D particle and energy transport

Stochastic baths: ideal gases at fixed temperature and chemical potential

T_L μ_L



T_R μ_R

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

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

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

$$\beta = 1/T$$

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

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

$$\Delta T = T_R - T_L$$

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:

$$J_q \propto J_\rho$$

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

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

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

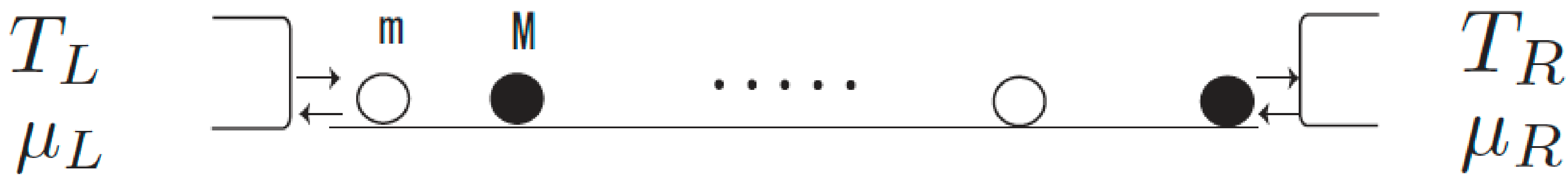
Carnot efficiency

Delta-like energy-filtering mechanism

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

1D interacting classical gas

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



For $M = m$

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

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

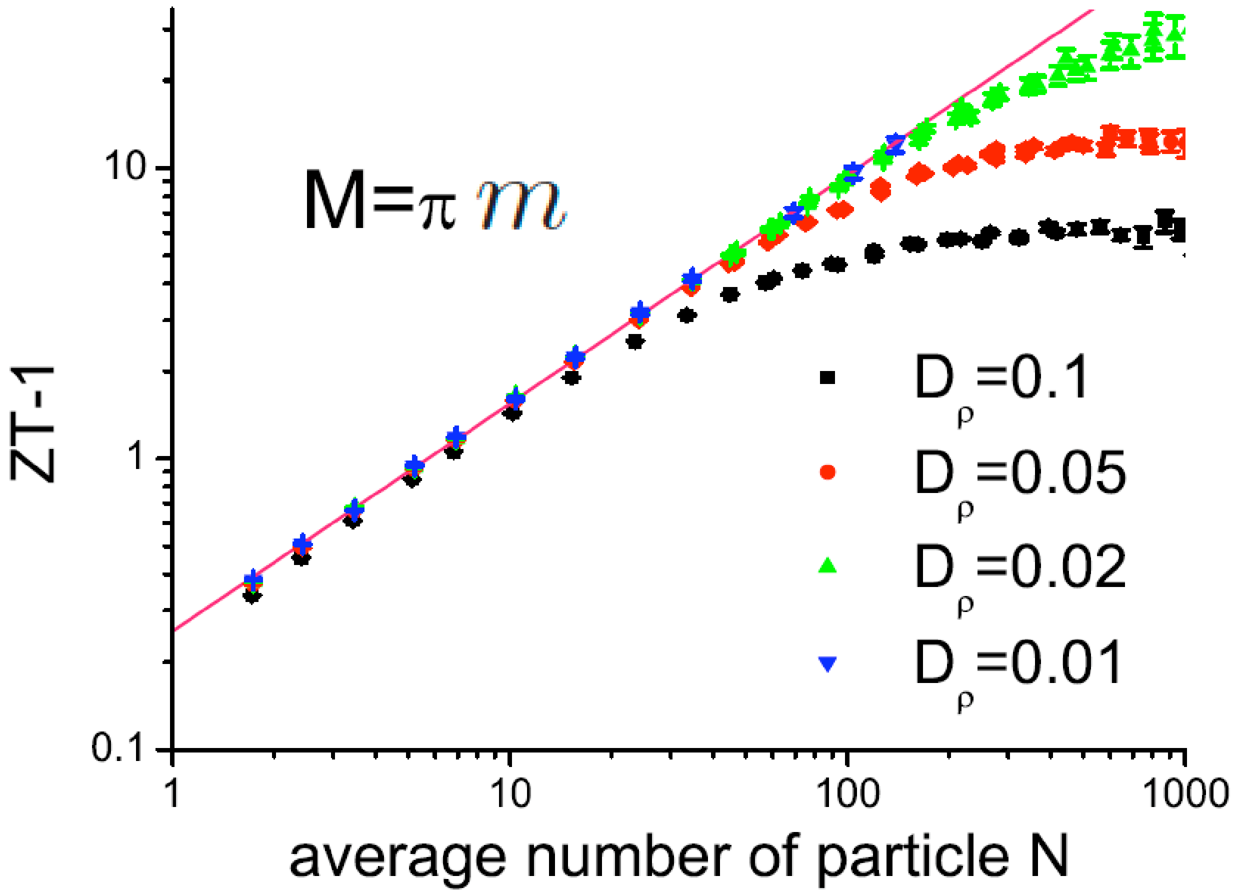
ZT =1

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

injection rates

For $M \neq m$ ZT depends on the number N of particles

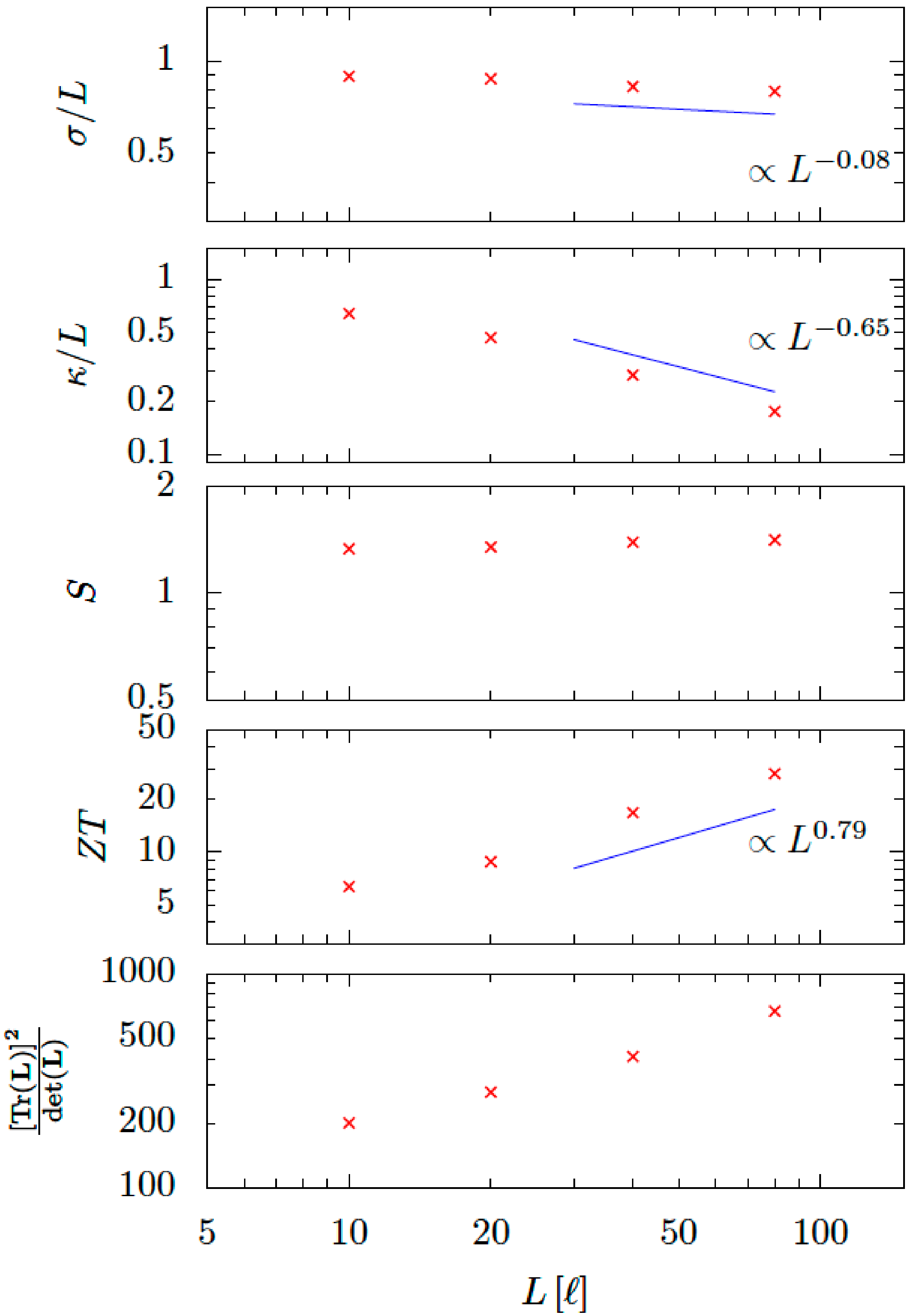
ZT diverges with increasing number of particles



$$ZT \propto N^{0.79}$$

$D_\rho = (\rho_R - \rho_L)/(\rho_R + \rho_L)$
relative density gradient

[Casati, Wang, Prosen, J. Stat. Mech. (2009) L03004]



ANOMALOUS TRANSPORT

Energy-filtering mechanism?

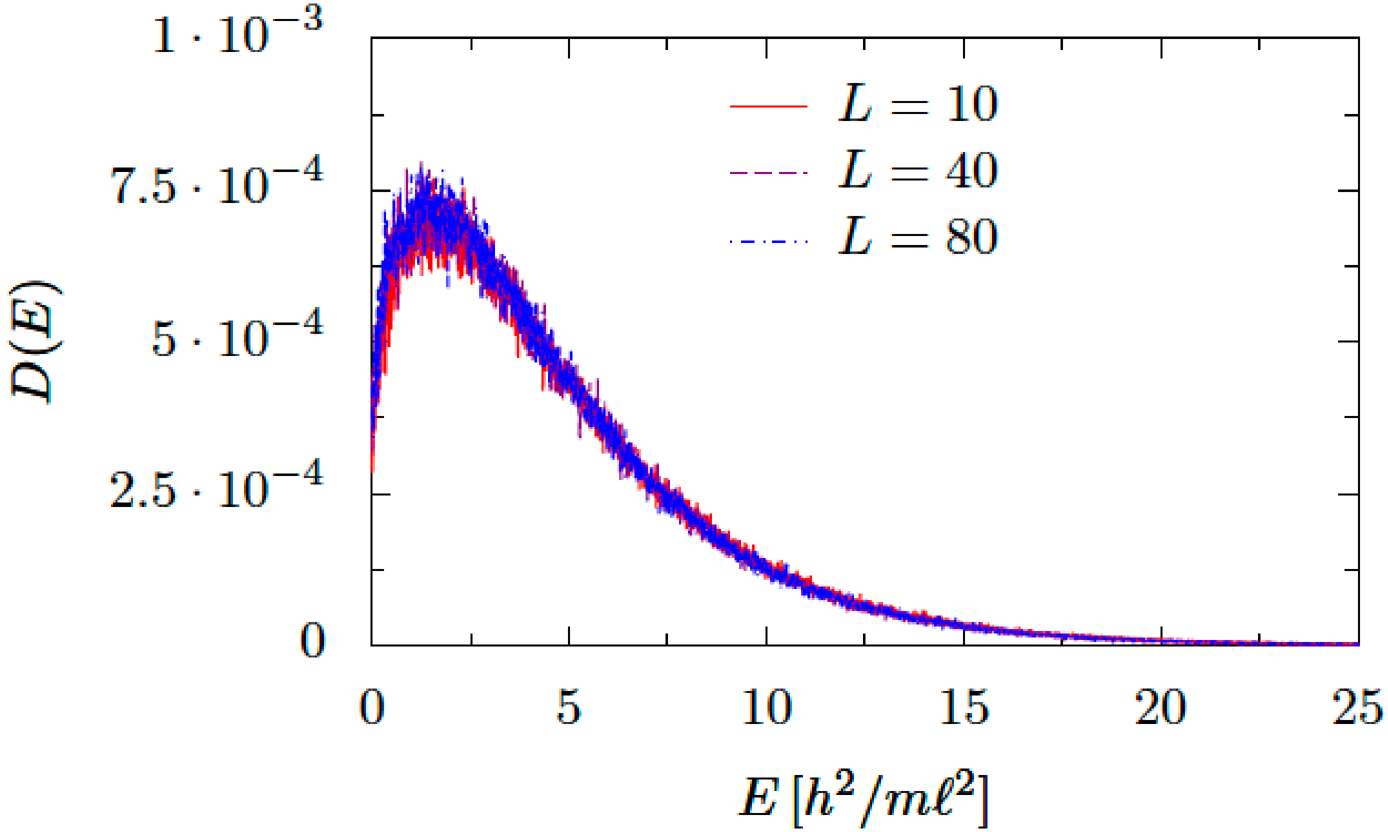
At a given position x compute:

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

$D(E) \equiv D_L(E) - D_R(E)$ **"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 different mechanism for increasing ZT is needed

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

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

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

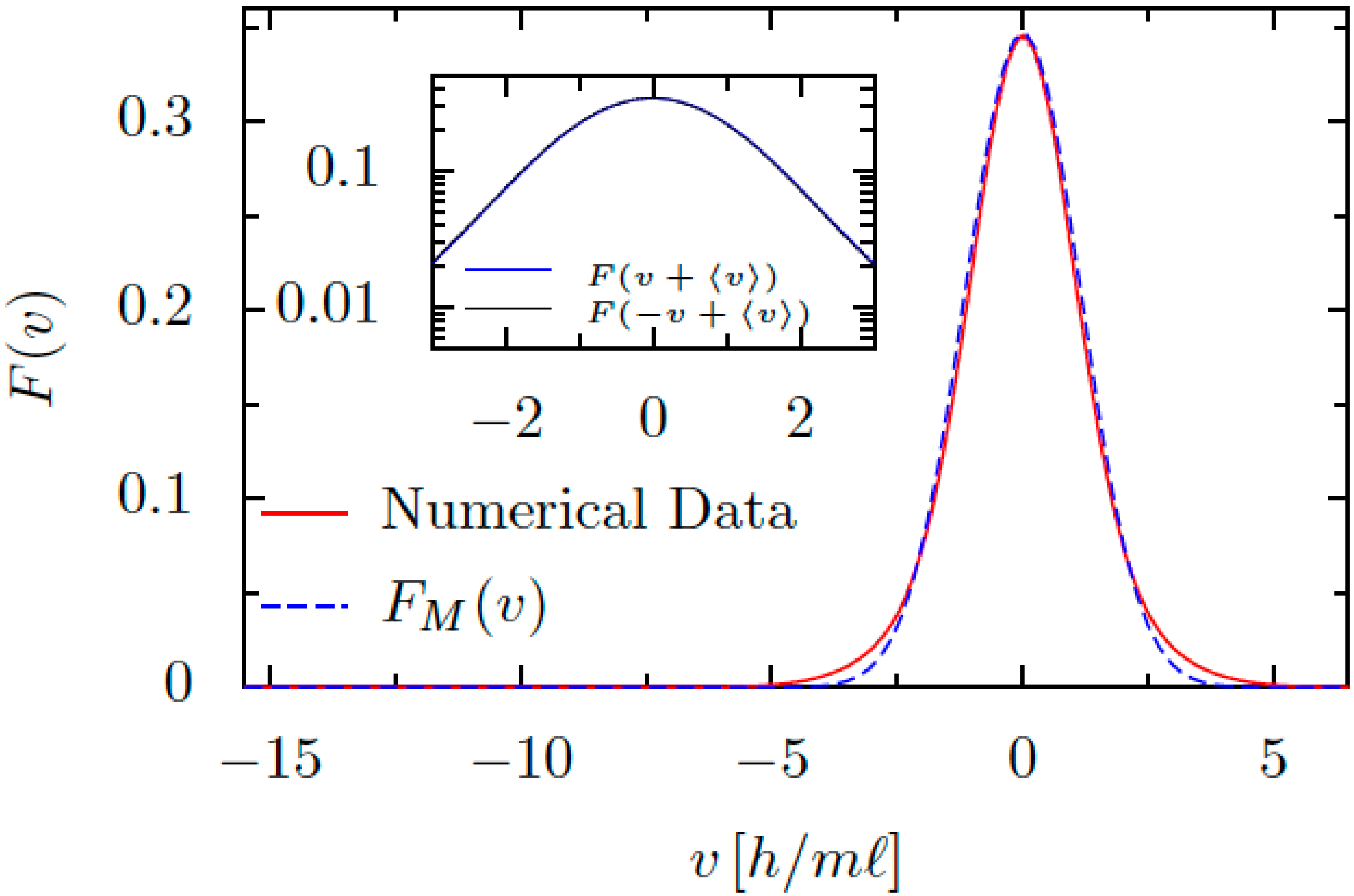
ZT diverges when $J_u \propto J_\rho \quad (J_u = J_q + \mu J_\rho)$

$$\Longrightarrow \qquad \overline{v^3} \propto \overline{v}$$

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

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

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

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

<u>Broad velocity distribution</u> 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 and Time-Reversal Breaking

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

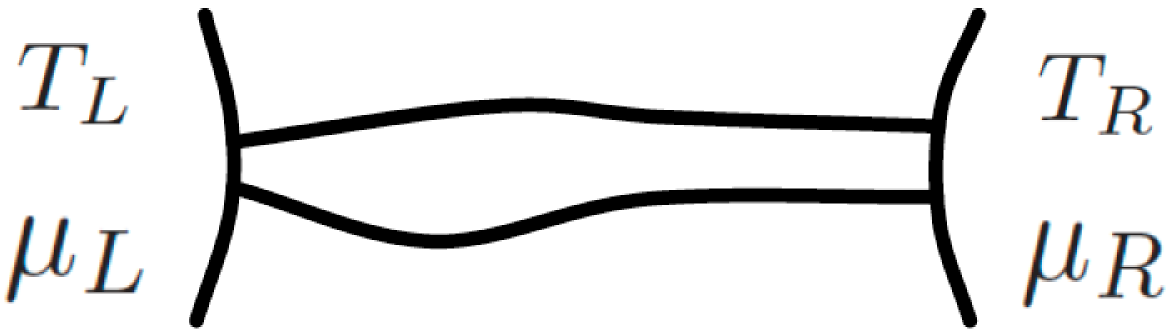
MAXIMUM EFFICIENCY

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

EFFICIENCY AT MAXIMUM POWER

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

And when time-reversal is broken?



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

$$X_1 = -\beta \Delta\mu$$
$$X_2 = \Delta\beta = -\Delta T / T^2$$
$$\beta = 1/T$$
$$\Delta\mu = \mu_R - \mu_L$$
$$\Delta\beta = \beta_R - \beta_L$$
$$\Delta T = T_R - T_L$$

B applied magnetic field or any parameter breaking time-reversibility

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

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

$\eta_C = -\Delta T/T$ 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

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

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

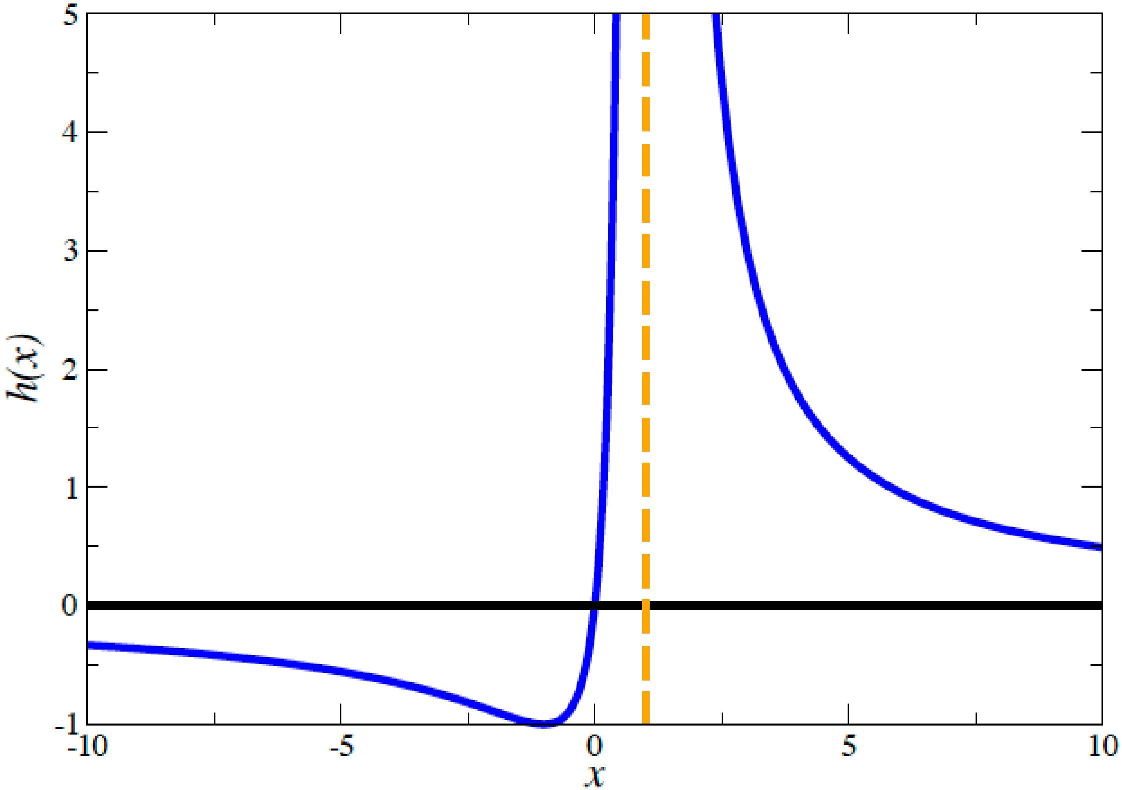
$$\eta(\omega_{\max}) = \frac{\eta_C}{2} \frac{xy}{2+y}$$

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

asymmetry parameter $x = 1$

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

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



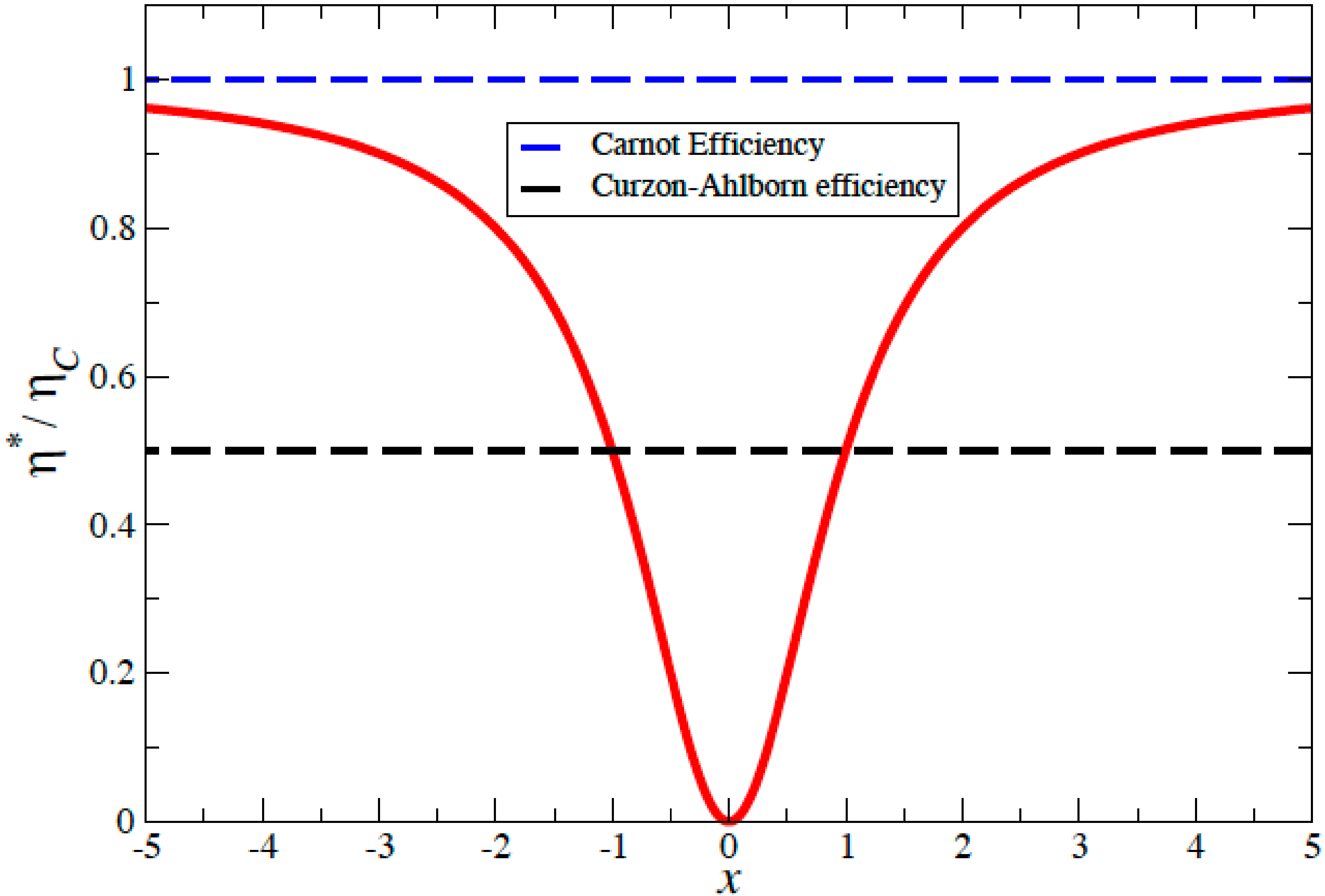
$$h(x) = 4x/(x-1)^2$$

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

achieved for $y = h(x)$

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

The Curzon-Ahlborn limit can be overcome within linear response



MAXIMUM EFFICIENCY

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

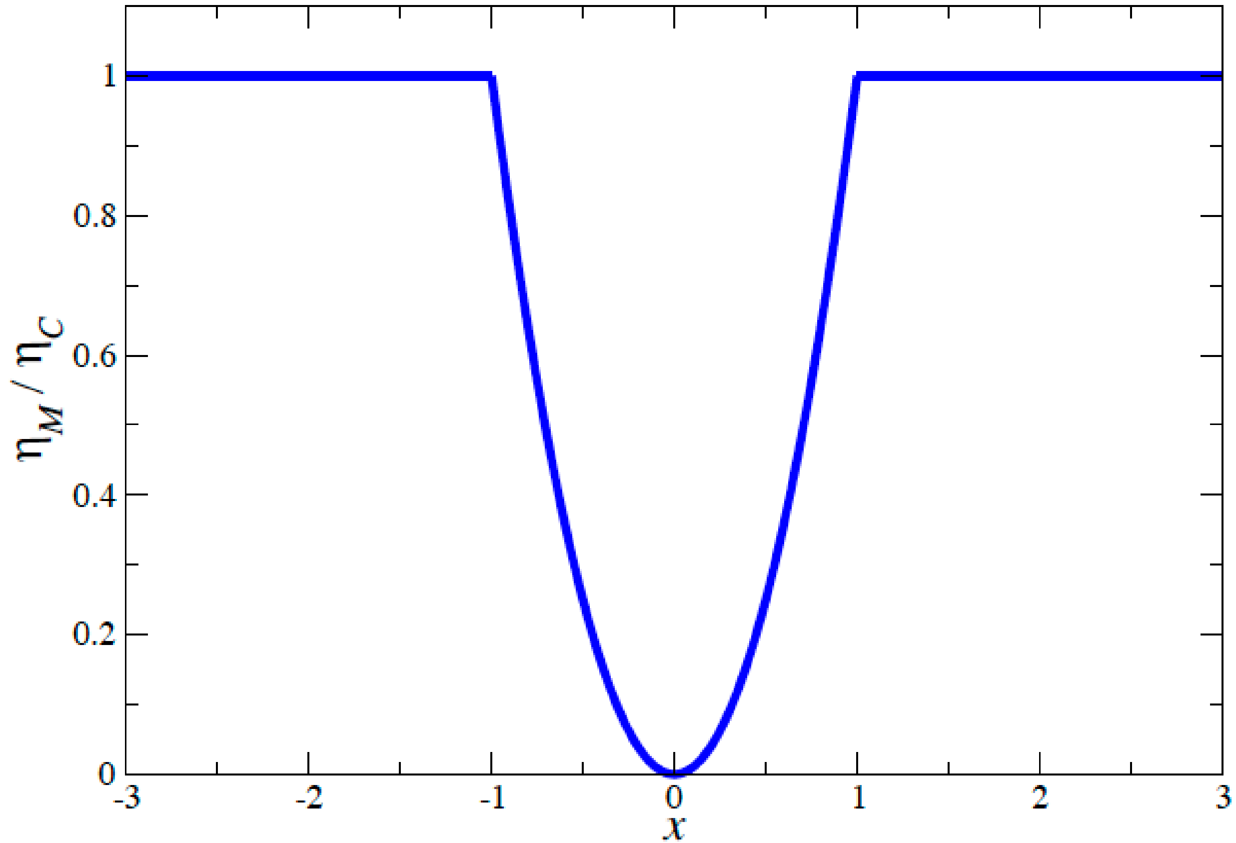
Maximum efficiency achieved for

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

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

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

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



The Carnot limit can be achieved only when

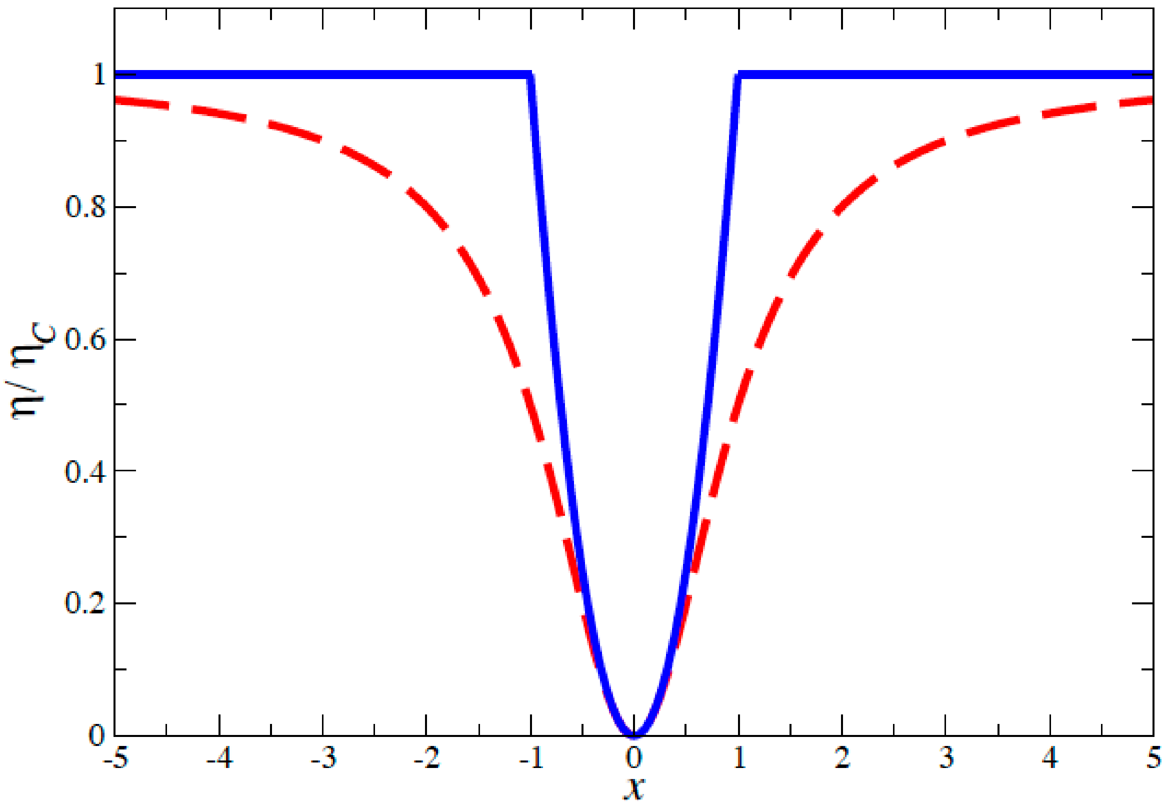
$$|x| \ge 1$$

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

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, is it possible to have simultaneously Carnot efficiency and non-zero power?



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

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

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

Maximum power at the maximum (Carnot) efficiency

Final remarks

1) Entropy production rate at maximum efficiency

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

2) For a refrigerator

$$\eta^{(r)} = J_q/\omega, \text{ with } J_q < 0,\ \omega < 0$$

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