CENTER FOR NONLINEAR AND COMPLEX SYSTEMS
Como - Italy

Can we control the heat current?
from thermal diodes to thermoelectric efficiency

Benenti	Como
Prosen	Lubliana
Saito	Tokyo
W. Jiao	Xiamen
Monasterio	Madrid

A central issue in physics

A central issue in physics

What are the fundamental limits that thermodynamics imposes on the efficiency of thermal machines?

A central issue in physics

What are the fundamental limits that thermodynamics imposes on the efficiency of thermal machines?

This problem is becoming more and more practically relevant in the future society due to the need of providing a sustainable supply of energy and to strong concerns about the environmental impact of the combustion of fossil fuels

Sadi Carnot, ***Reflexions Sur la Puissance Motrice du Feu et Sur Les Machines Propres a` Developper Cette Puissance*** **(Bachelier, Paris, 1824).**

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In a cycle between two reservoirs at temperatures T_1 and T_2 ($T_1 > T_2$), the efficiency η_C is bounded by the so-called Carnot efficiency

$$\eta = W/Q_1 \leq \eta_C = 1 - T_2/T_1$$

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The Carnot efficiency is obtained for a quasistatic transformation which requires infinite time and therefore the extracted power, in this limit, reduces to zero.

Efficiency at maximum power

$$\eta_{CA} = 1 - \sqrt{T_2/T_1}$$

Curzon -Ahlborn upper bound

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- Thermoelectric efficiency

Can one derive the Fourier law of heat conduction from dynamical equations of motion without any statistical assumptions?

J. B. FOURIER

1808 - Attempt to explain the thermal gradient inside the earth

Heat flow obyes a simple diffusive equation which can be regarded as the continuum limit of a discrete random walk

Randonmnes is an essential ingredient of thermal conductivity

VOLUME 52, NUMBER 21 PHYSICAL REVIEW LETTERS 21 MAY 1984

One-Dimensional Classical Many-Body System Having a Normal Thermal Conductivity

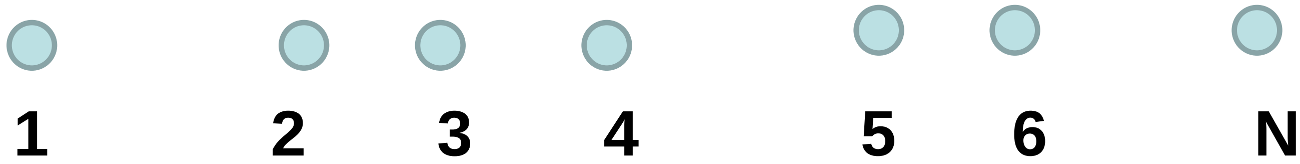
G.C. J. Ford, F. Vivaldi, W.M. Visscher

deterministically random systems are tacitly required by the transport theory

THE DING-A -LING MODEL

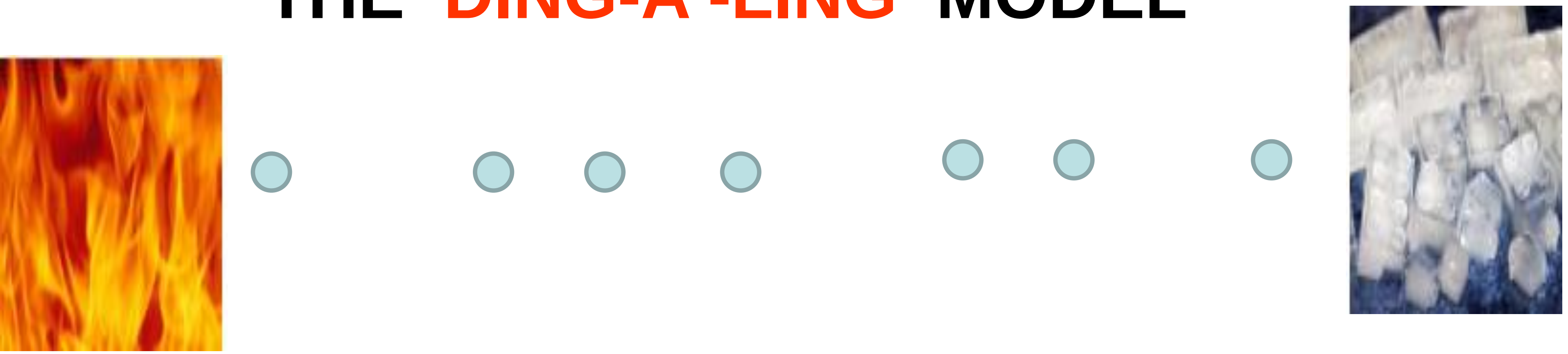
Particles collide elastically.

Even particles harmonically bounded



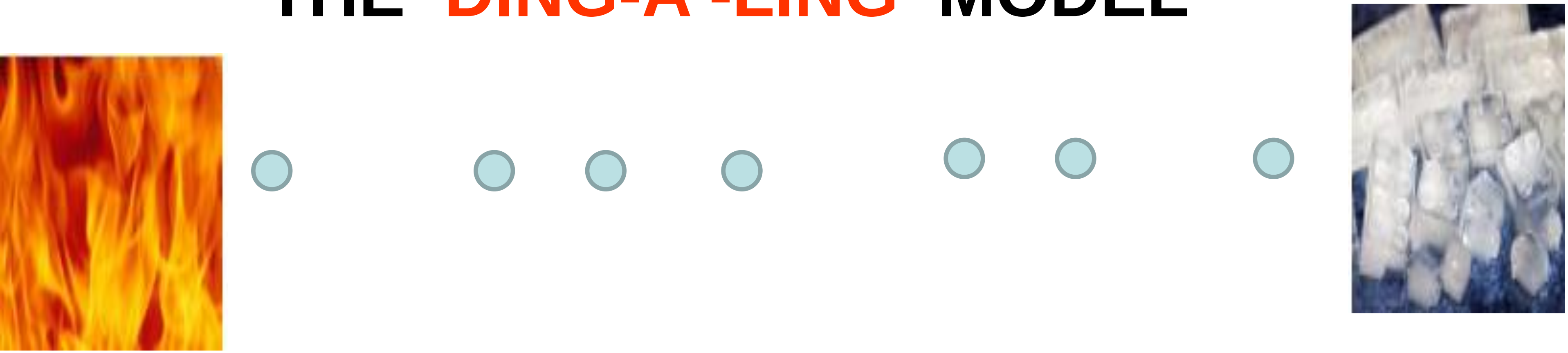
Strong chaos for

THE DING-A -LING MODEL



Introduce thermal baths

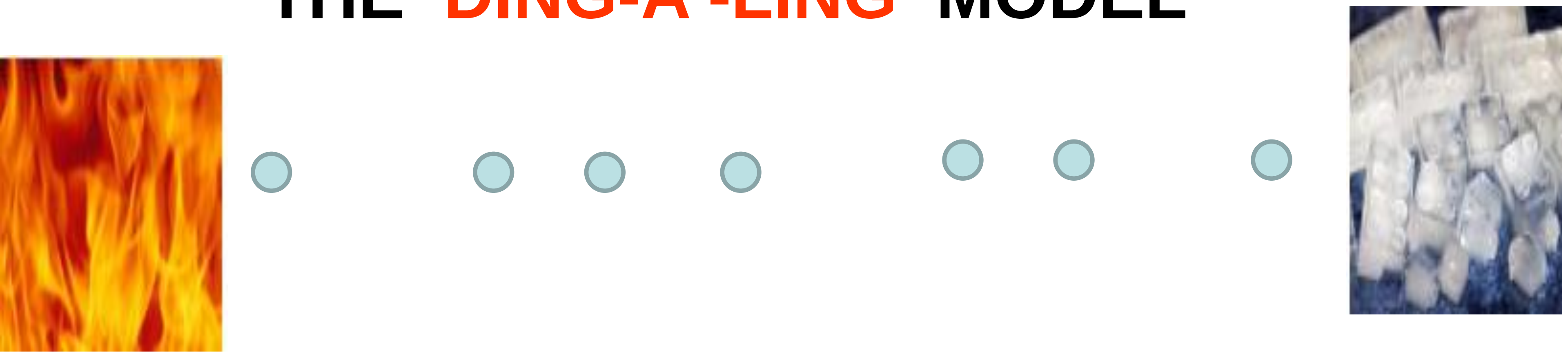
THE DING-A -LING MODEL



Introduce thermal baths

Compute internal temperature

THE DING-A -LING MODEL

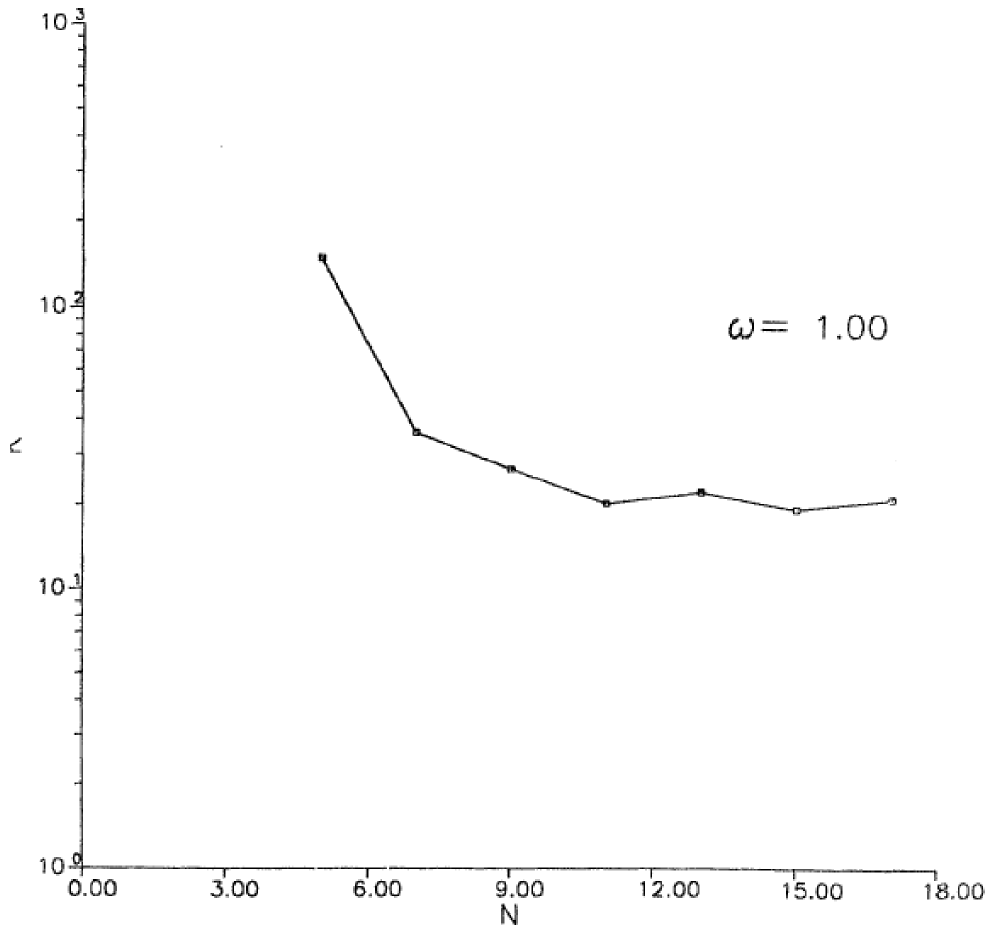


Introduce thermal baths

Compute internal temperature

Compute heat flux

One-Dimensional Classical Many-Body System Having a Normal Thermal Conductivity



G.C. J. Ford, F. Vivaldi, W.M. Visscher prl 52, 1861 (1984)

Fourier's law obeyed — official

Analysis of a mechanical model characterized by deterministic randomness (chaos) allows verification of elementary principles of heat conduction. But it may have other value.

materials. Whether reductionists should be alarmed by all this is quite a different matter, although some of them may be dismayed that this may be that hitherto elusive problem for which only computer solutions are attainable. **John Maddox**

Nature, 7 june 1984

FOURIER LAW IN QUANTUM MECHANICS?

Deterministic chaos appear to be an important ingredient for Fourier law.

No exponential instability in Quantum Mechanics

Terra Incognita

WIGNER - DYSON THEORY OF RANDOM MATRICES

Energy levels spacing distribution

RANDOM MATRIX THEORY

RANDOM MATRIX THEORY

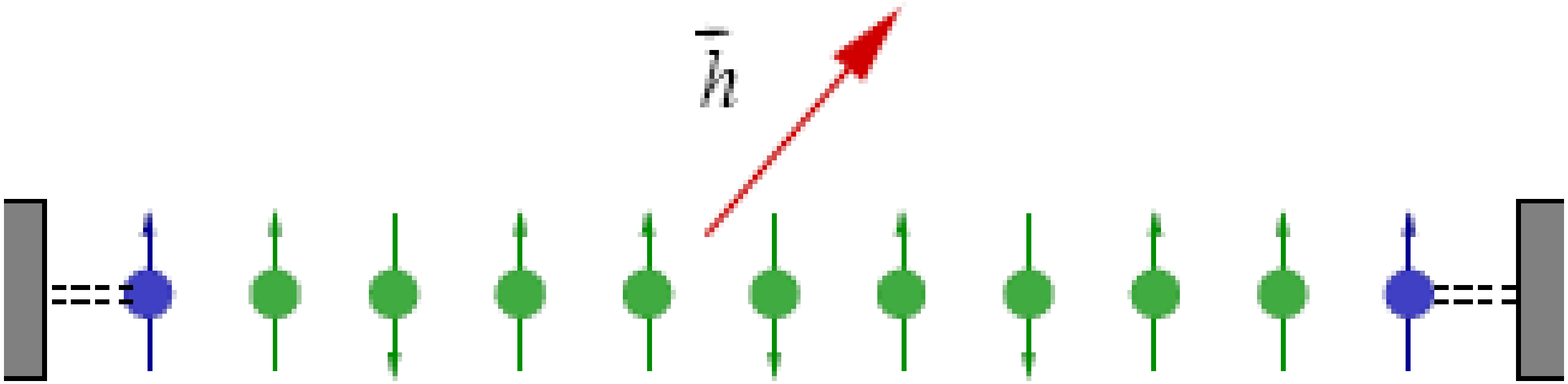
SIGNATURES OF QUANTUM CHAOS

For classically chaotic systems the distribution of energy levels spacings obeys the

Wigner-Dyson surmise

G.C., F. Valz_Gris, I. Guarneri: Lettere al Nuovo Cimento
28 (1980) 279

On the Connection between Quantization of Nonintegrable Systems and Statistical Theory of Spectra (*).

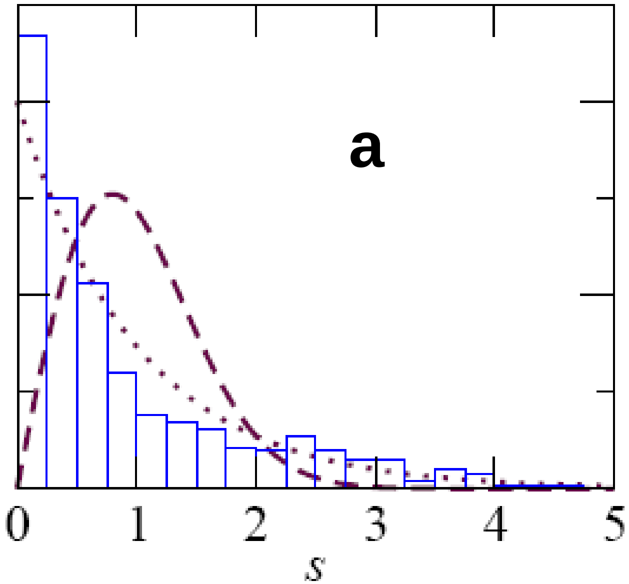


$$\mathcal{H} = -Q\sum_{n=0}^{L-2} \sigma_n^z \sigma_{n+1}^z + \vec{h}\cdot\sum_{n=0}^{L-1} \vec{\sigma}_n \ ,$$

$$\vec{h} = (h_x, 0, h_z)$$

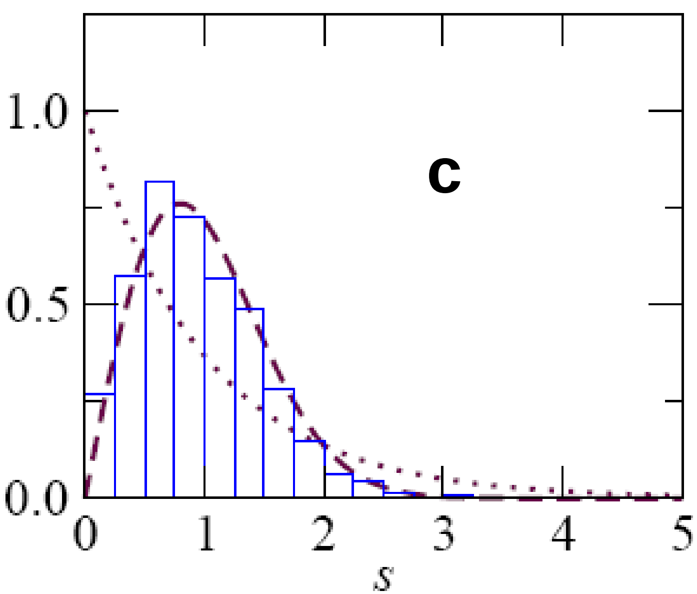
$$\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$$

G. Monasterio, T. Prosen, G.C.
EPL (2005)



a) Integrable ($h_x = 3.4$, $h_z = 0$)

$P(s) = \exp(-s)$



c) Chaotic ($h_x = 3.4$, $h_z = 2$)

$$P(s) = \frac{\pi}{2} s \exp\left(-\frac{\pi}{4} s^2\right)$$

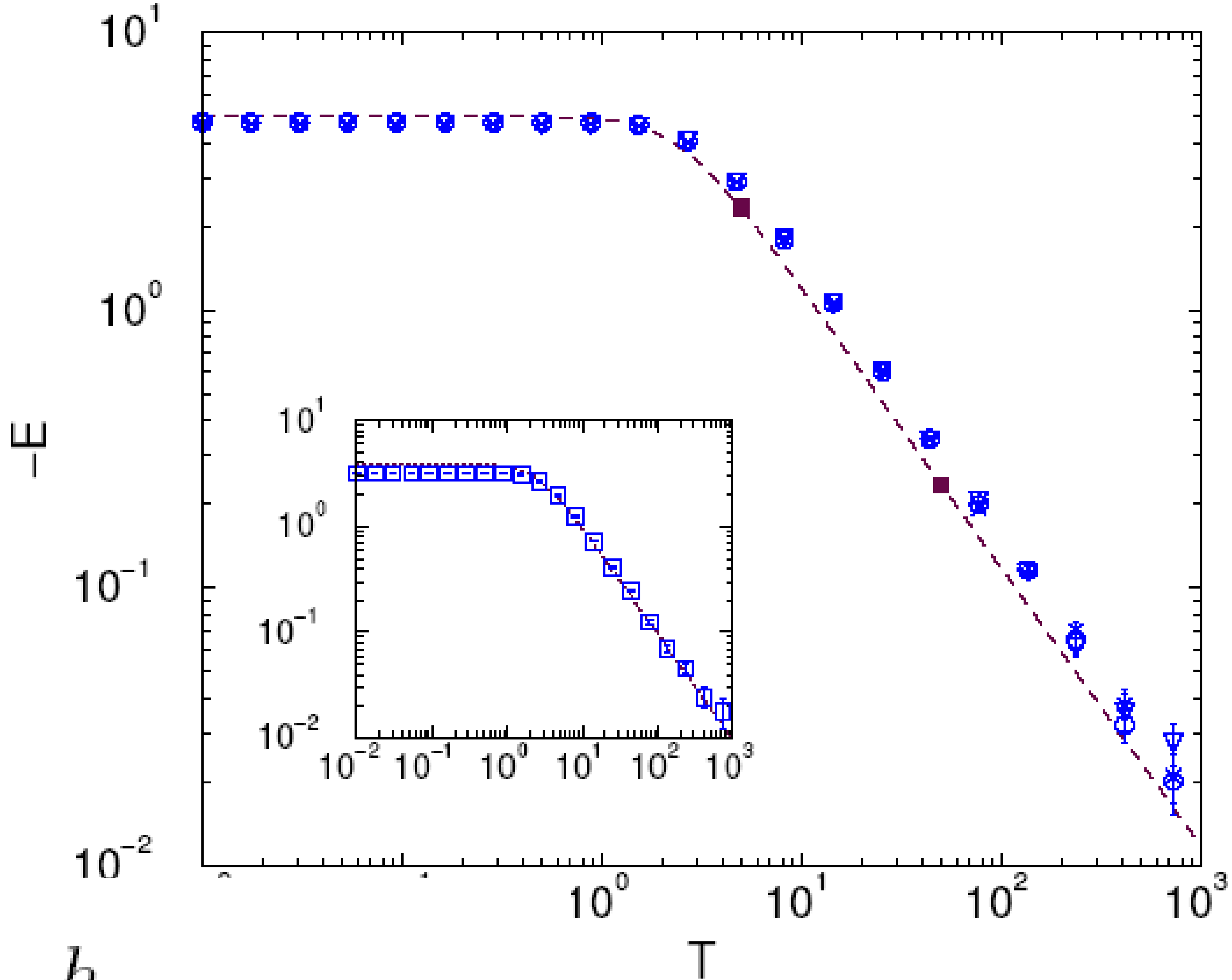
$$|\psi(t)\rangle = \sum_{s_0, s_1, \ldots, s_{L-1}} C_{s_0, s_1, \ldots, s_{L-1}}(t) |s_0, s_1 \ldots s_{L-1}\rangle \ ,$$

End particles interact with baths at discrete times.
Their state is determined by Boltzmann distribution at temperature T.

$E = \langle H_n \rangle$

$E \sim 1/T$

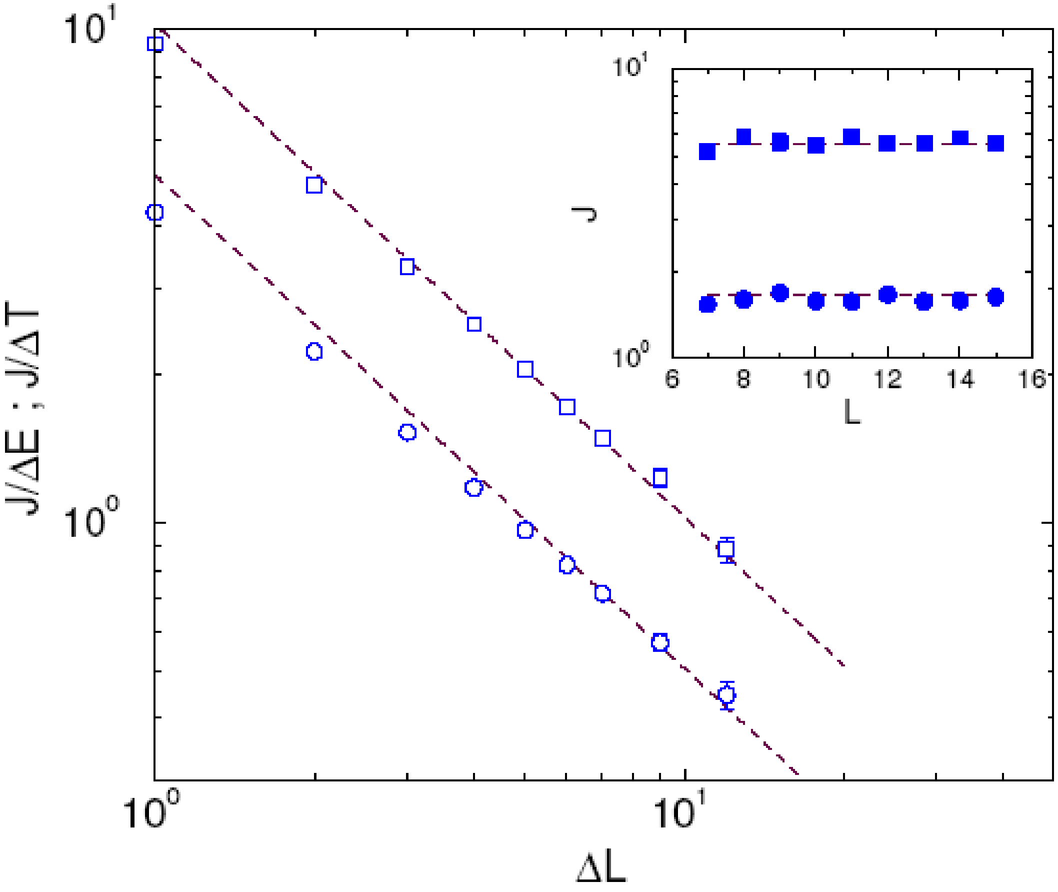
$T \simeq -1/E$



$$\mathcal{H} = \sum_{n=0}^{L-2} H_n + \frac{h}{2}(\sigma_1 + \sigma_r) \ .$$

$$H_n = -Q\sigma_n^z \sigma_{n+1}^z + \frac{\vec{h}}{2} \cdot (\vec{\sigma}_n + \vec{\sigma}_{n+1}) \ .$$

G. Monasterio, T. Prosen, G.C.   EPL (2005)



Can we control the heat current?

Towards thermal diodes and thermal transistors

M. Terraneo, M. Peyrard and G.C. p.r.l. 88, (2002)

$$H = \sum_{n=1,N} \frac{p_n^2}{2m} + V_n(y_n) + \frac{1}{2}K(y_n - y_{n-1})^2$$

$$V_n(y_n) = D_n(e^{-\alpha_n y_n} - 1)^2$$

$$H = \sum_{n=1,N} \frac{p_n^2}{2m} + V_n(y_n) + \frac{1}{2}K(y_n - y_{n-1})^2$$

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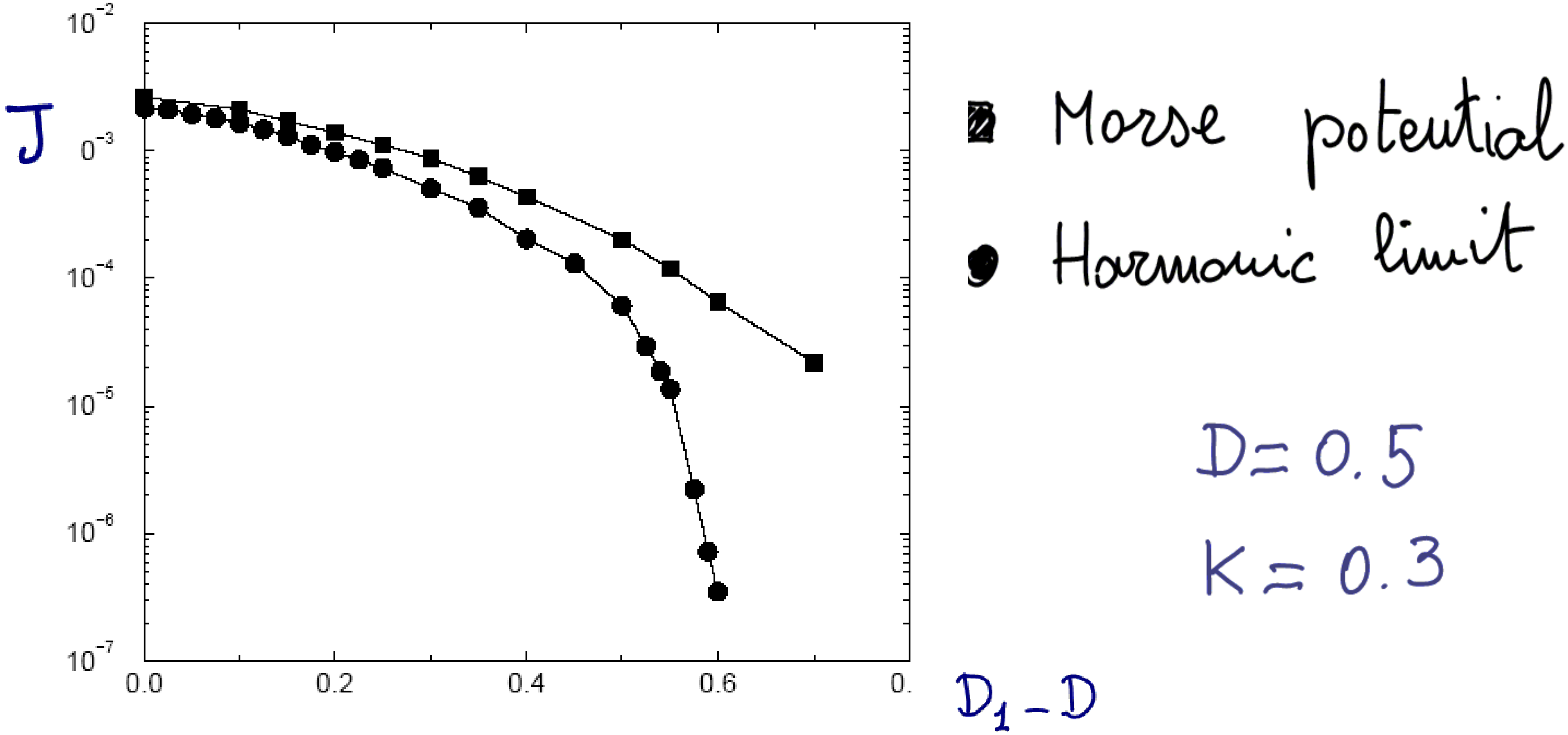

J
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
0.0
0.2
0.4
0.6
0.
$D_1 - D$
Morse potential
Harmonic limit
D = 0.5
K = 0.3

$$H = \sum_{i=n,N} \frac{p_n^2}{2m} + \tilde{D}_n y_n^2 + \frac{1}{2} K(y_n - y_{n-1})^2$$

$$y_n(t) = e^{ikn - i\omega t}$$

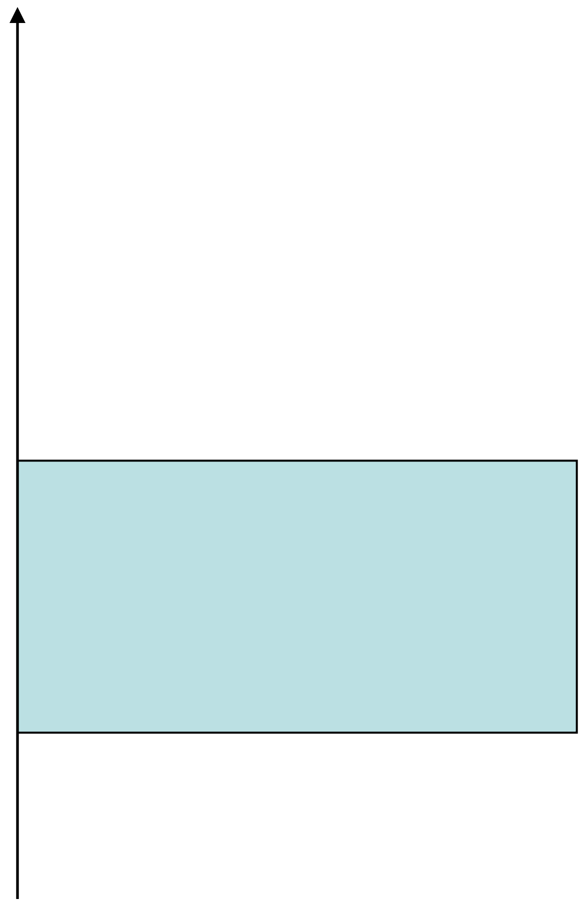
Plane waves solutions

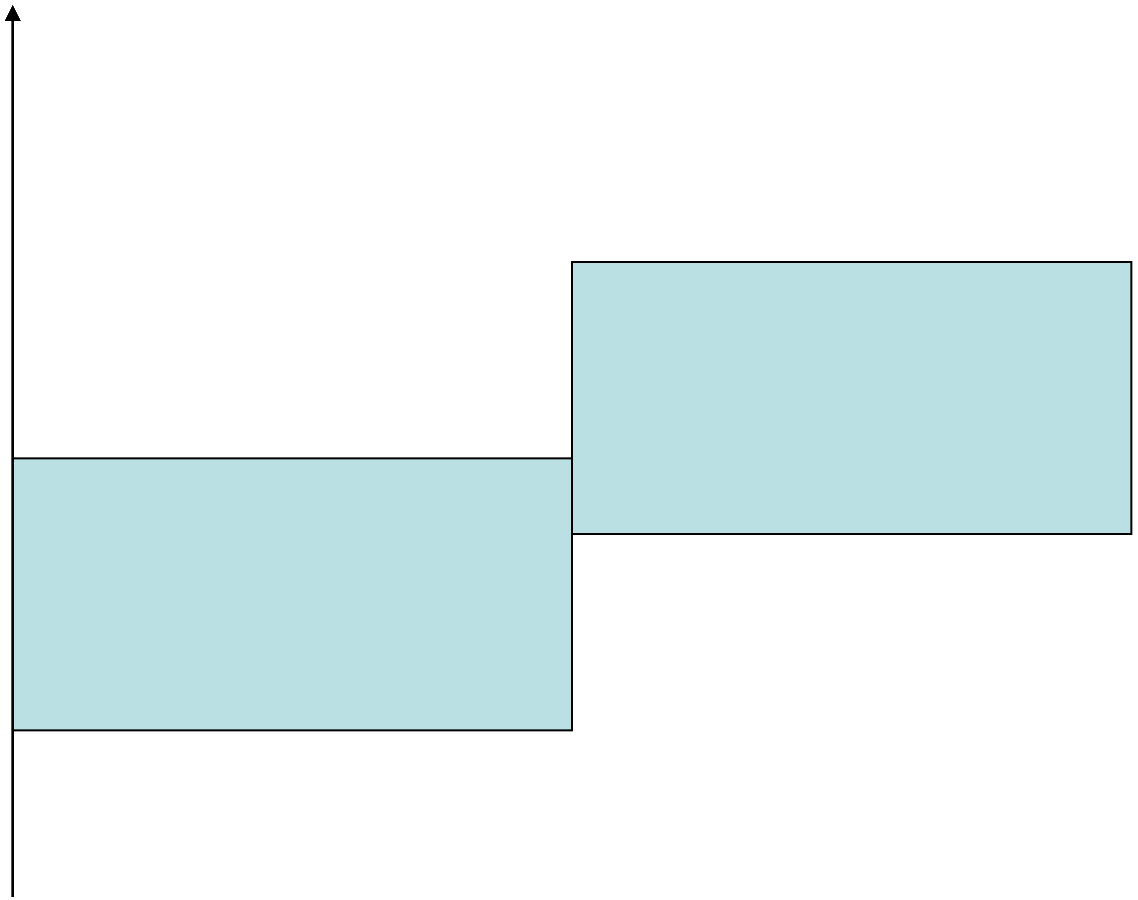
$$\omega^2 = 2K + 2\tilde{D} - 2K \cos k$$

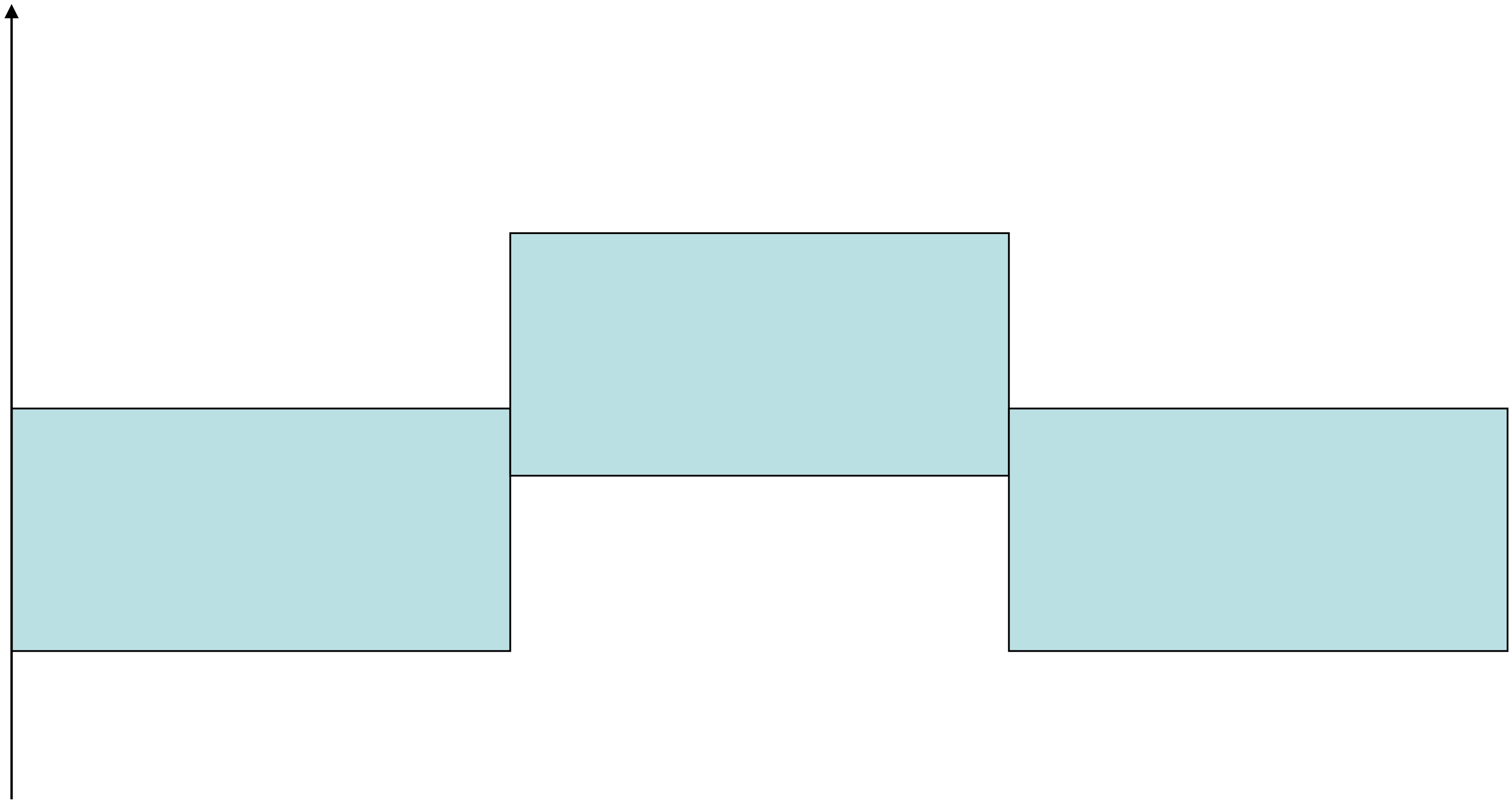
Dispersion relations

$$2\tilde{D} \leq \omega^2 \leq 2\tilde{D} + 4K$$

Phonon band

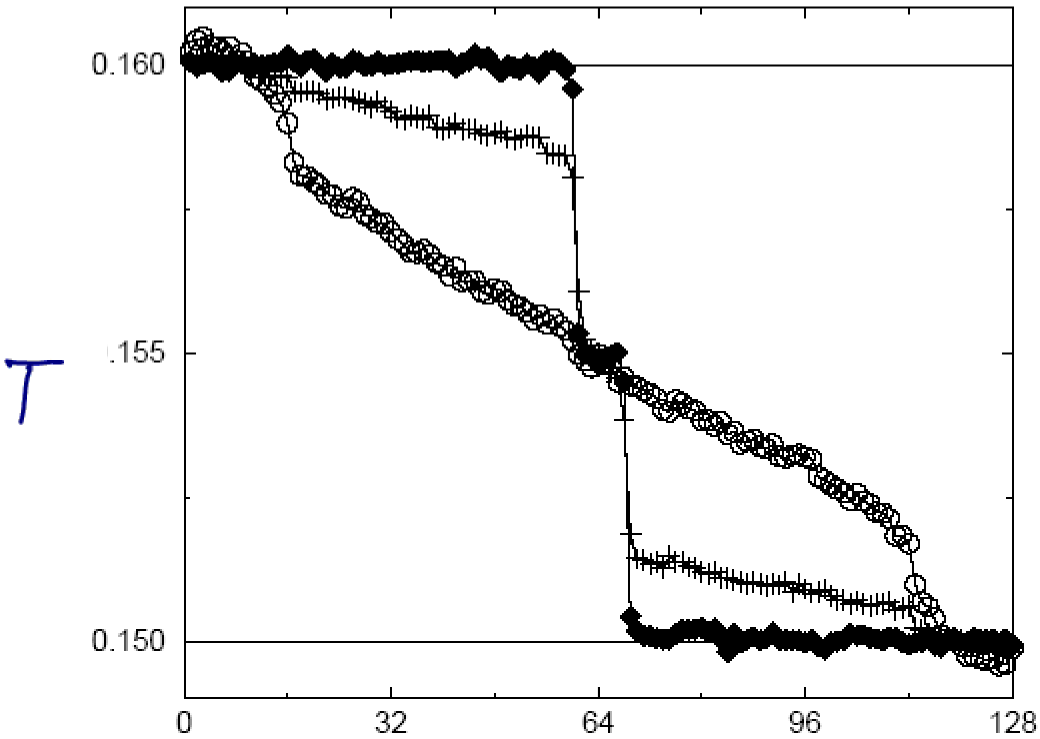






INTERNAL TEMPERATURE PROFILE

$D = 0.5$



$(K = 0.3)$

$(\alpha_n = \alpha = 1)$

$$H = \sum_{n=1,N} \frac{p_n^2}{2m} + V_n(y_n) + \frac{1}{2}K(y_n - y_{n-1})^2$$

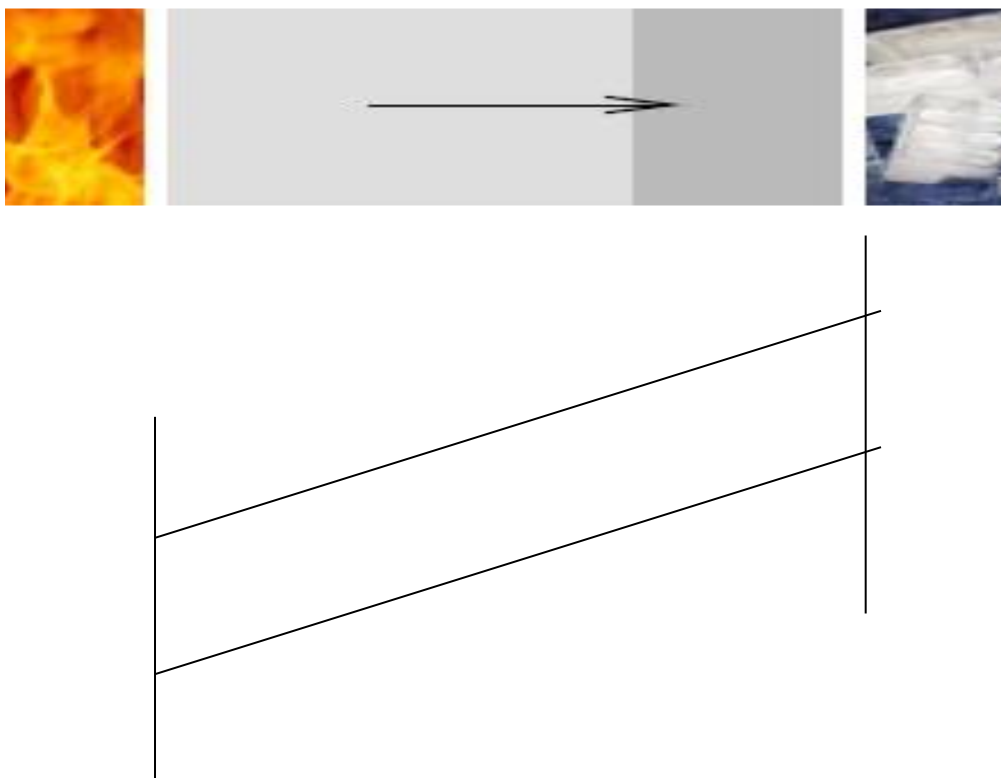
$$V_n(y_n) = D_n(e^{-\alpha_n y_n} - 1)^2$$

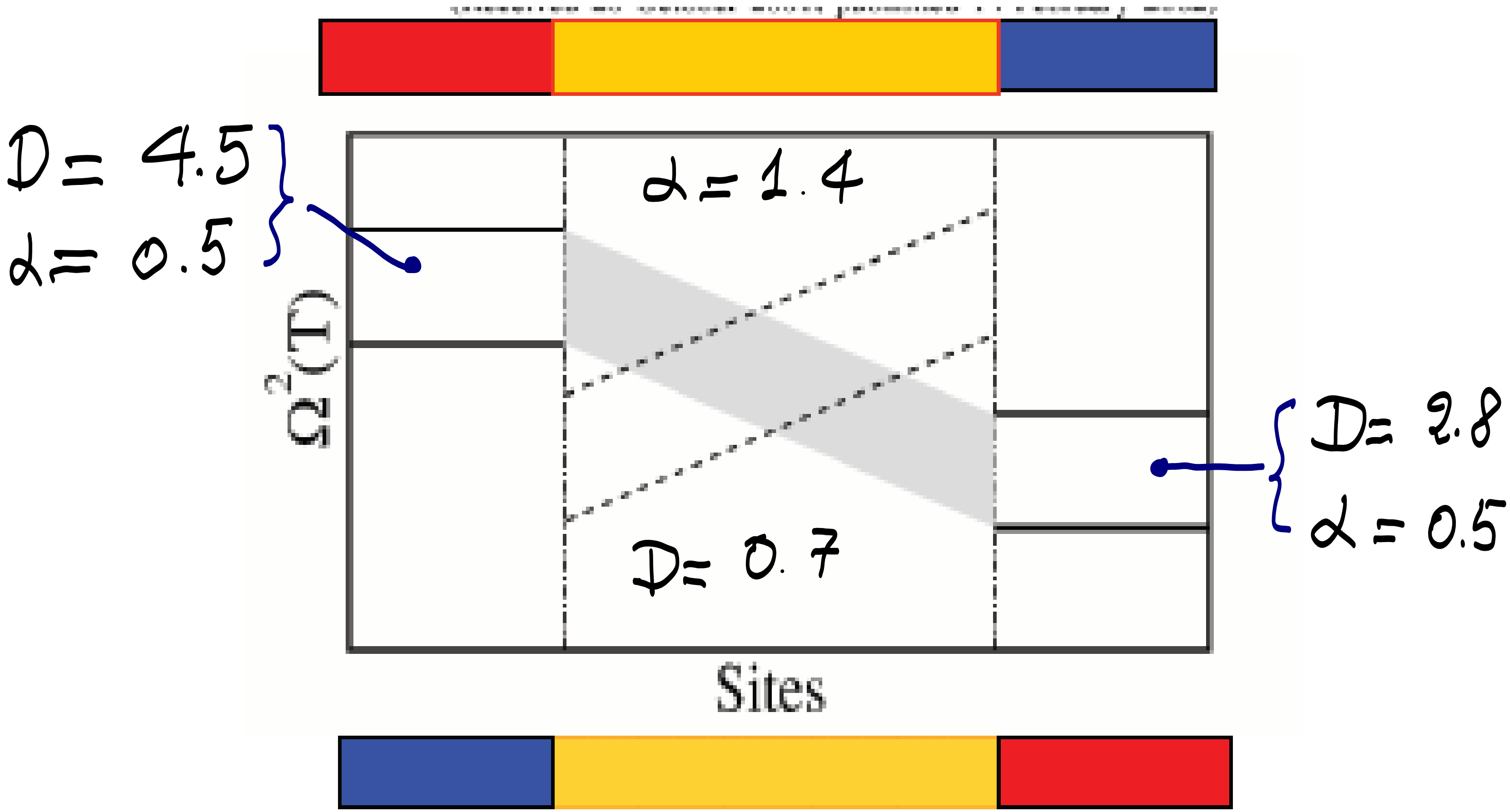
Break symmetry!

M. Terraneo, M. Peyrard and G.C. p.r.l. 88, (2002)

In nonlinear systems the position of the band depends on the temperature

$$V_n(y_n) = D_n(e^{-\alpha_n y_n} - 1)^2$$





M. Terraneo, M. Peyrard and G.C. p.r.l. 88, (2002)

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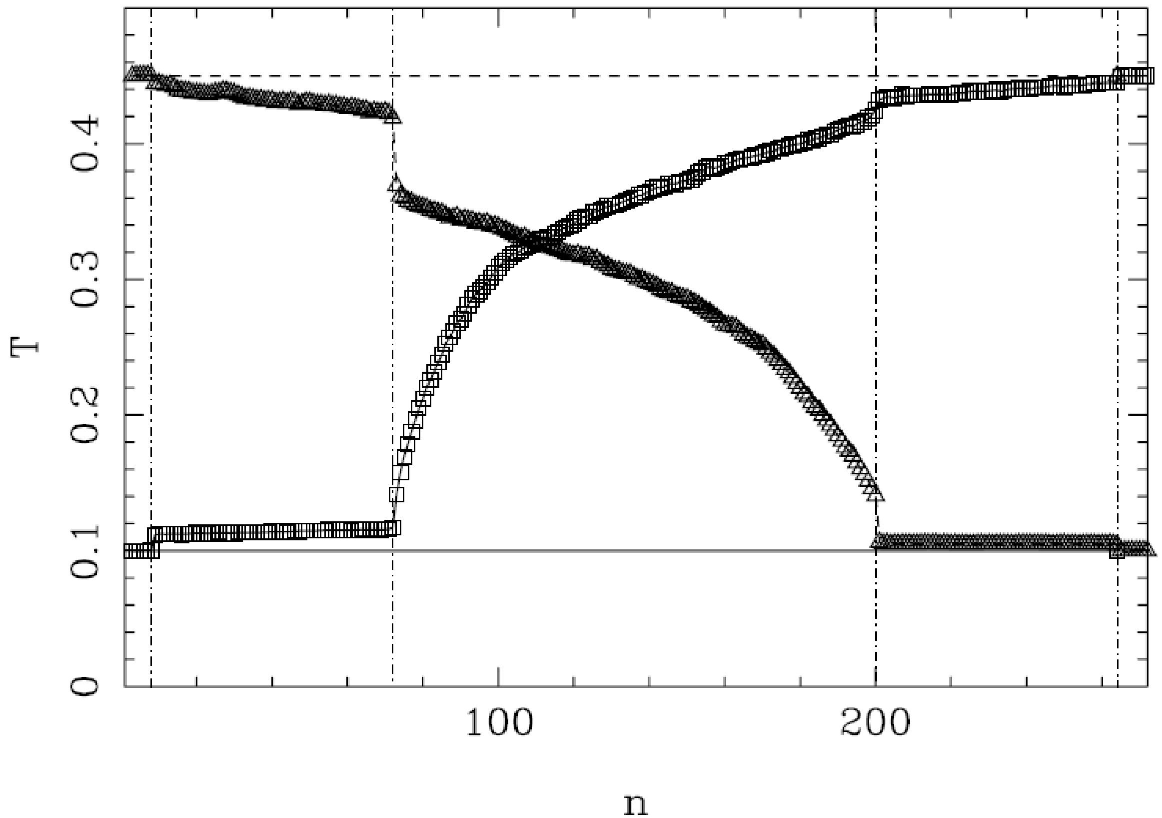


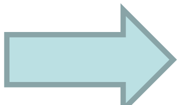
Internal temperature profile

Average flux

High temperature on the rigth side:

High temperature on the left side:

Rectification factor:

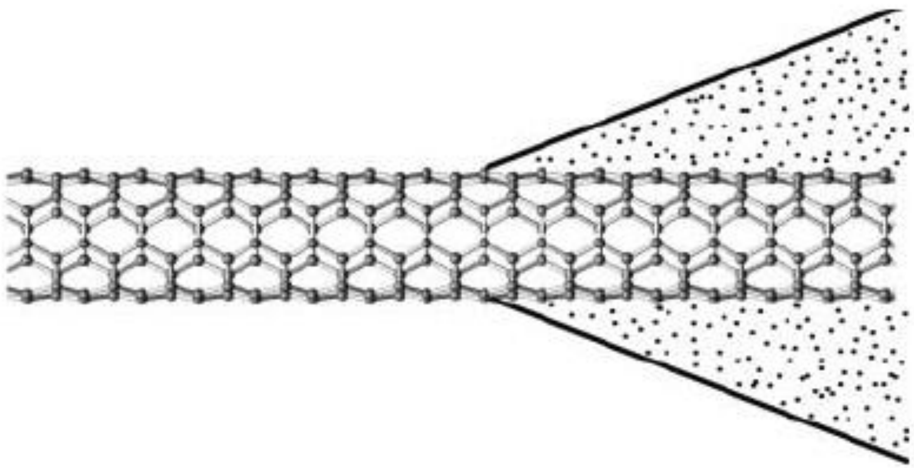


Discontinuities at interfaces **bad energy transfer**

Solid-State Thermal Rectifier

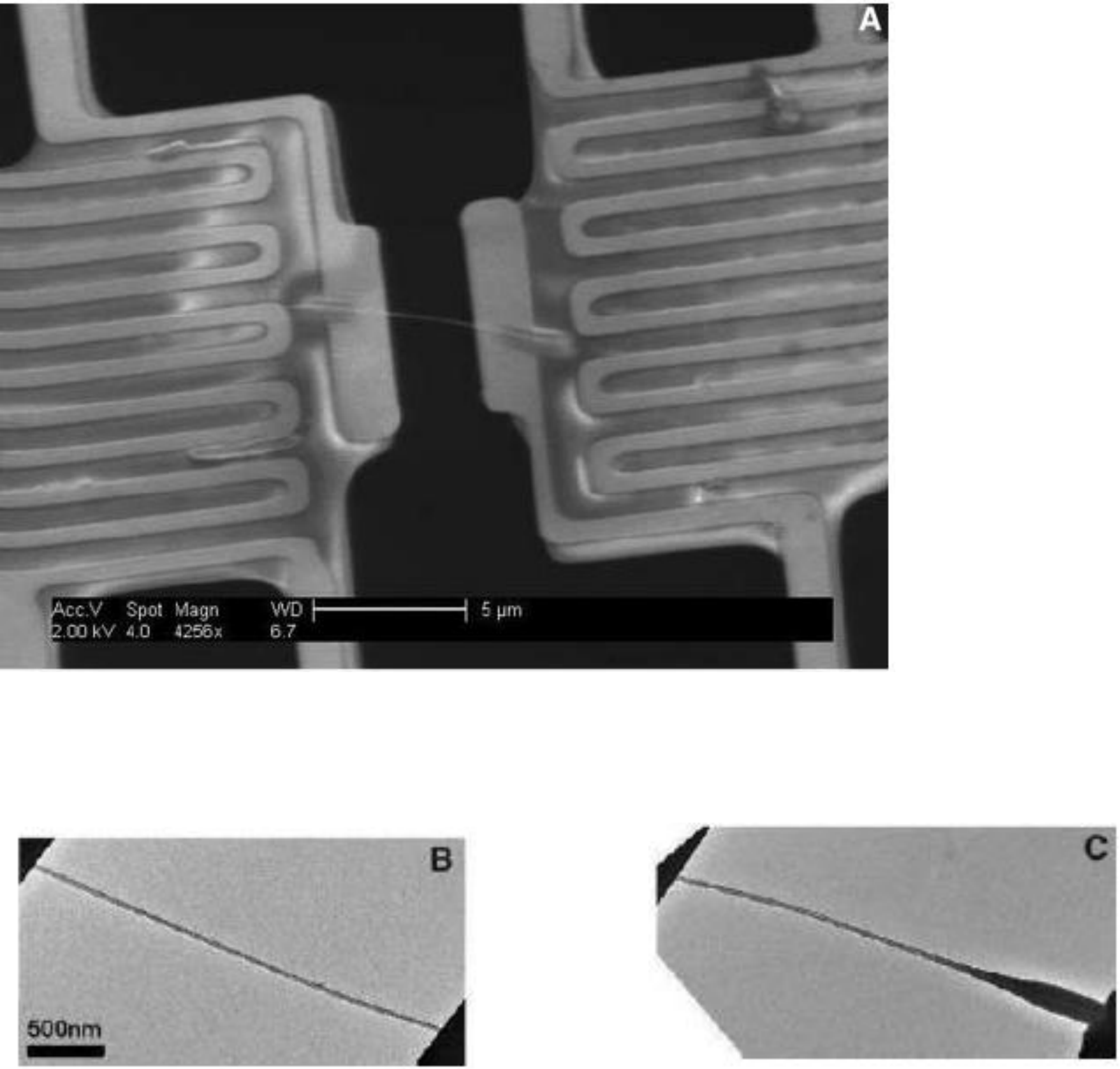
C. W. Chang,[1,4] D. Okawa,[1] A. Majumdar,[2,3,4] A. Zettl[1,3,4]*

SCIENCE VOL 314 17 NOVEMBER 2006

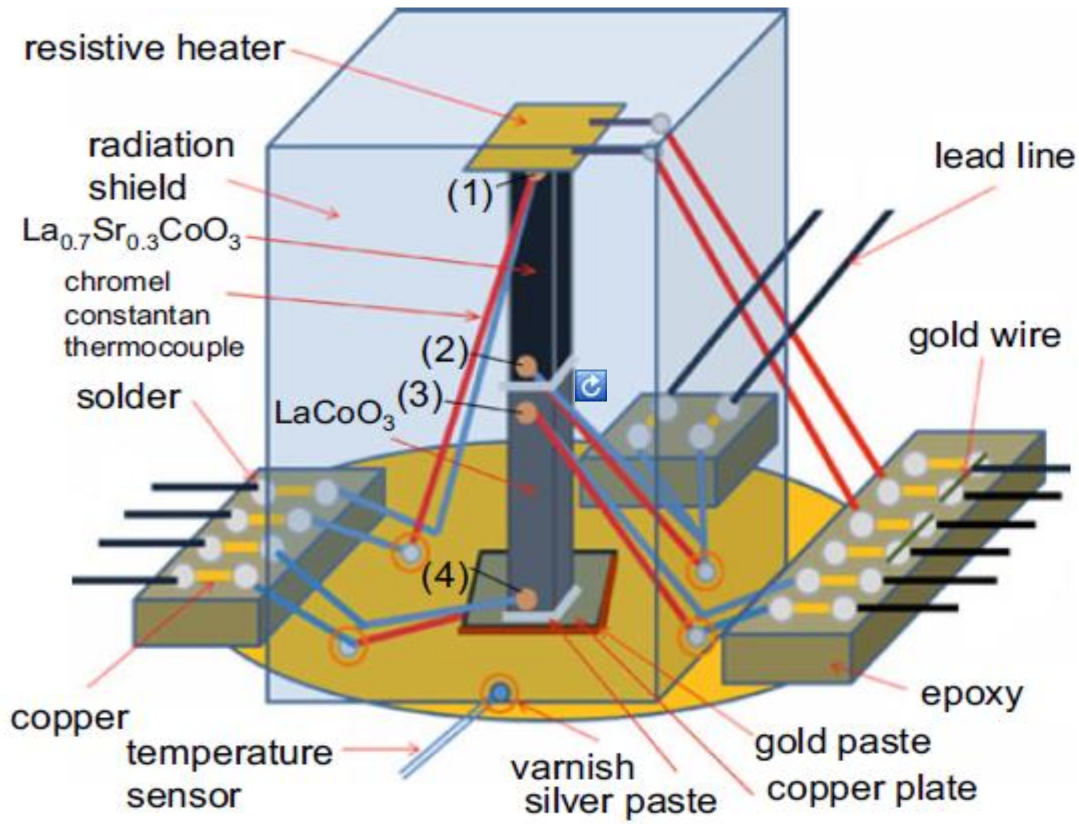


For uniform mass distribution, thermal conduction is symmetric.

For mass loading geometry higher thermal conductance was observed when heat flowed from the high-mass region to the low –mass region.


A
Acc.V Spot Magn WD 5 µm
2.00 kV 4.0 4256x 6.7
B
500nm
C

W. KOBAYASHI, Y. TERAOKA, and I. TERASAKI,
"Journal of Electronics Materials", 2010

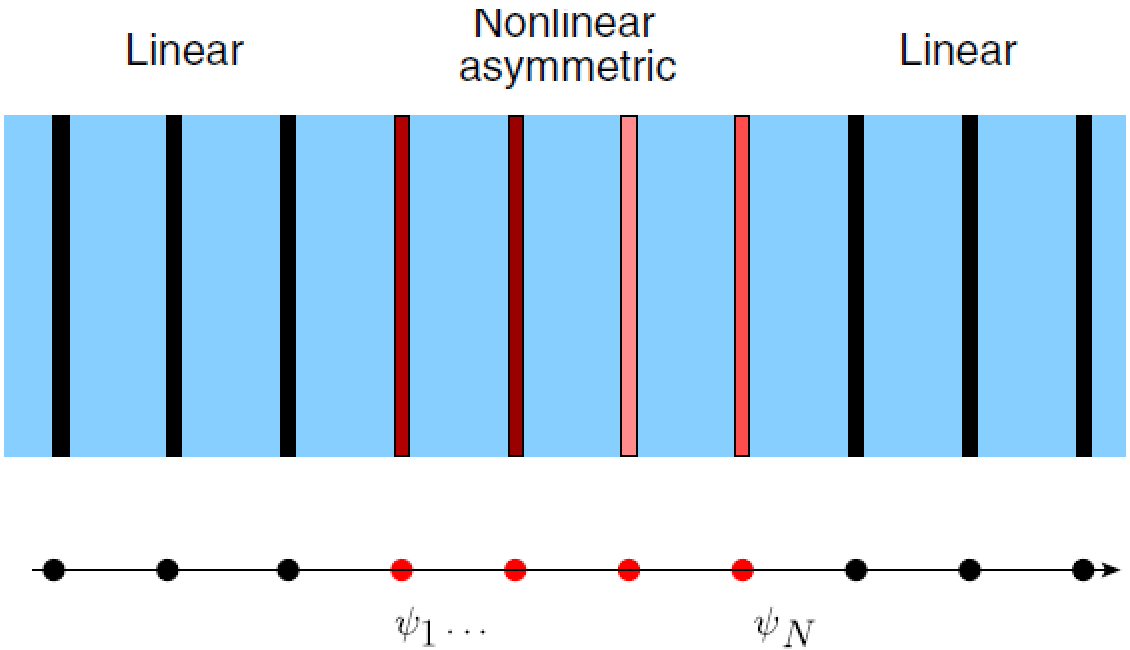


Thermal conductivity depends on temperature

G.C., S. Lepri, prl. 106, 164101 (2011)

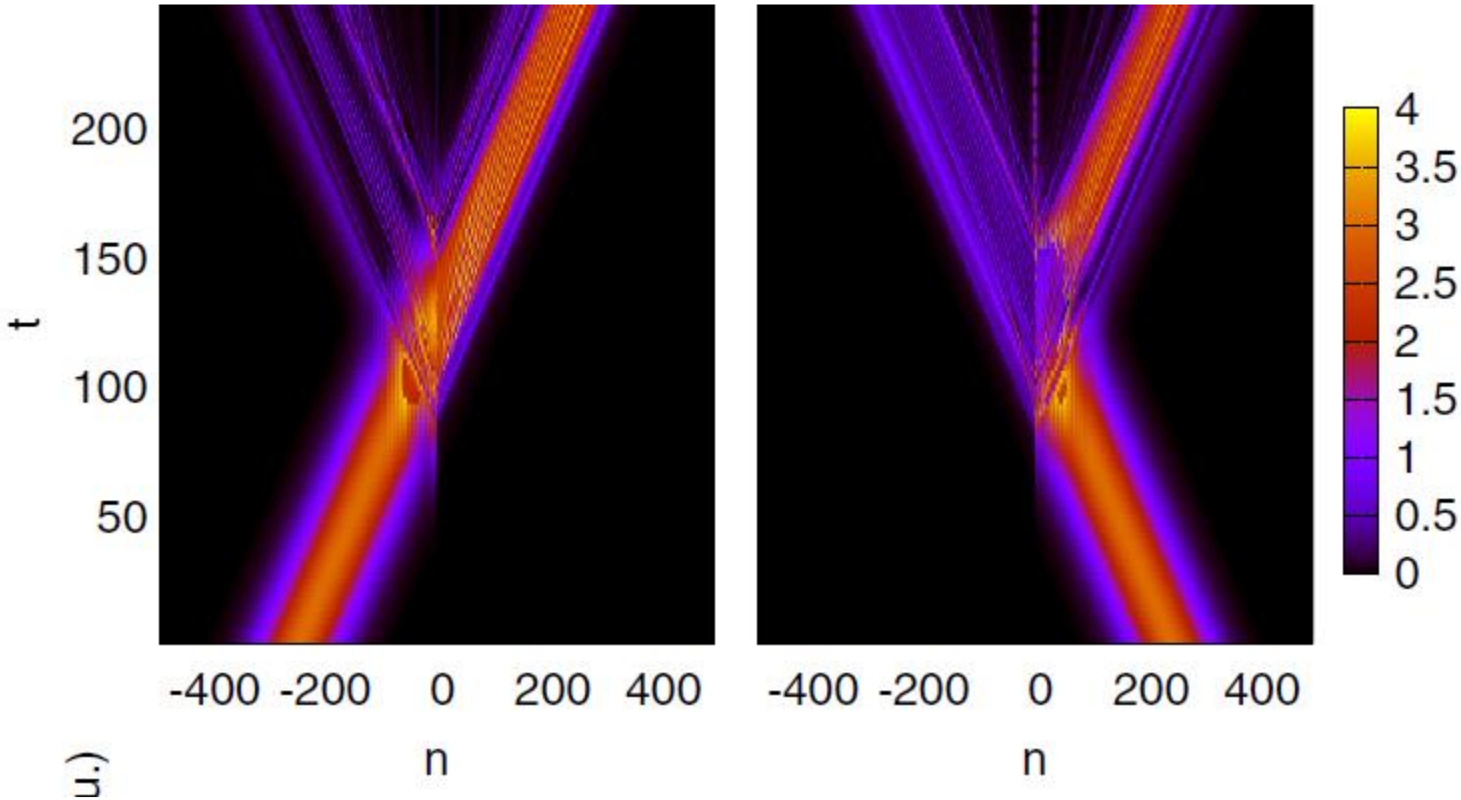
A wave diode: asymmetric wave propagation in nonlinear systems

Layered photonic(phononic) crystal

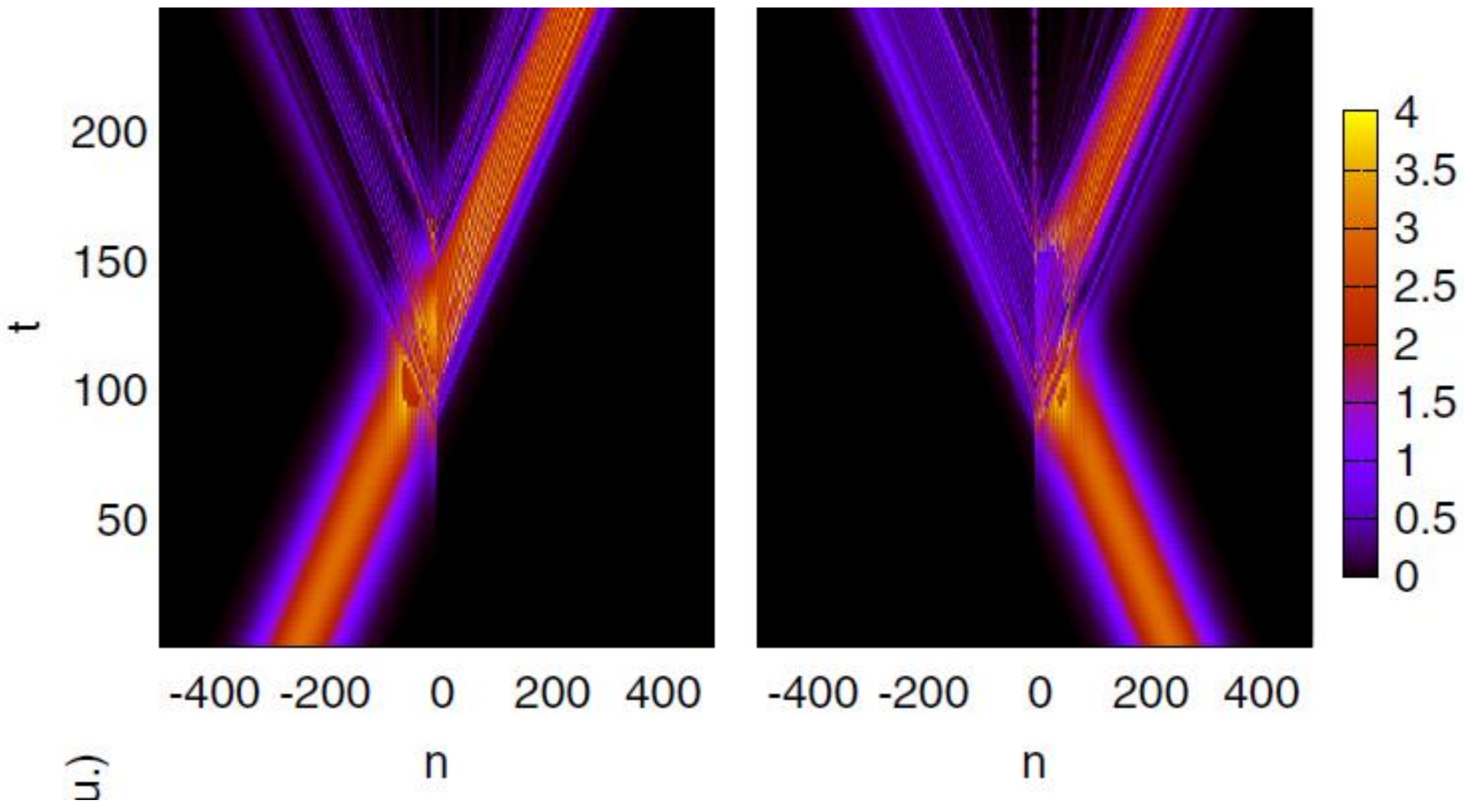


$$\omega \psi_n = V_n \psi_n - \psi_{n+1} - \psi_{n-1} + \alpha_n |\psi_n|^2 \psi_n$$

G.C., S. Lepri, prl. 106, 164101 (2011)



The transmission is large for the left incoming packet



We solve numerically the time-dependent DNLS on a finite lattice with open b.c.

$$i\dot{\phi}_n = V_n\phi_n - \phi_{n+1} - \phi_{n-1} + \alpha_n|\phi_n|^2\phi_n$$

Initial condition a Gaussian packet

$$\phi_n(0) = I\exp\left[-\frac{(n-n_0)^2}{w} + ik_0 n\right].$$

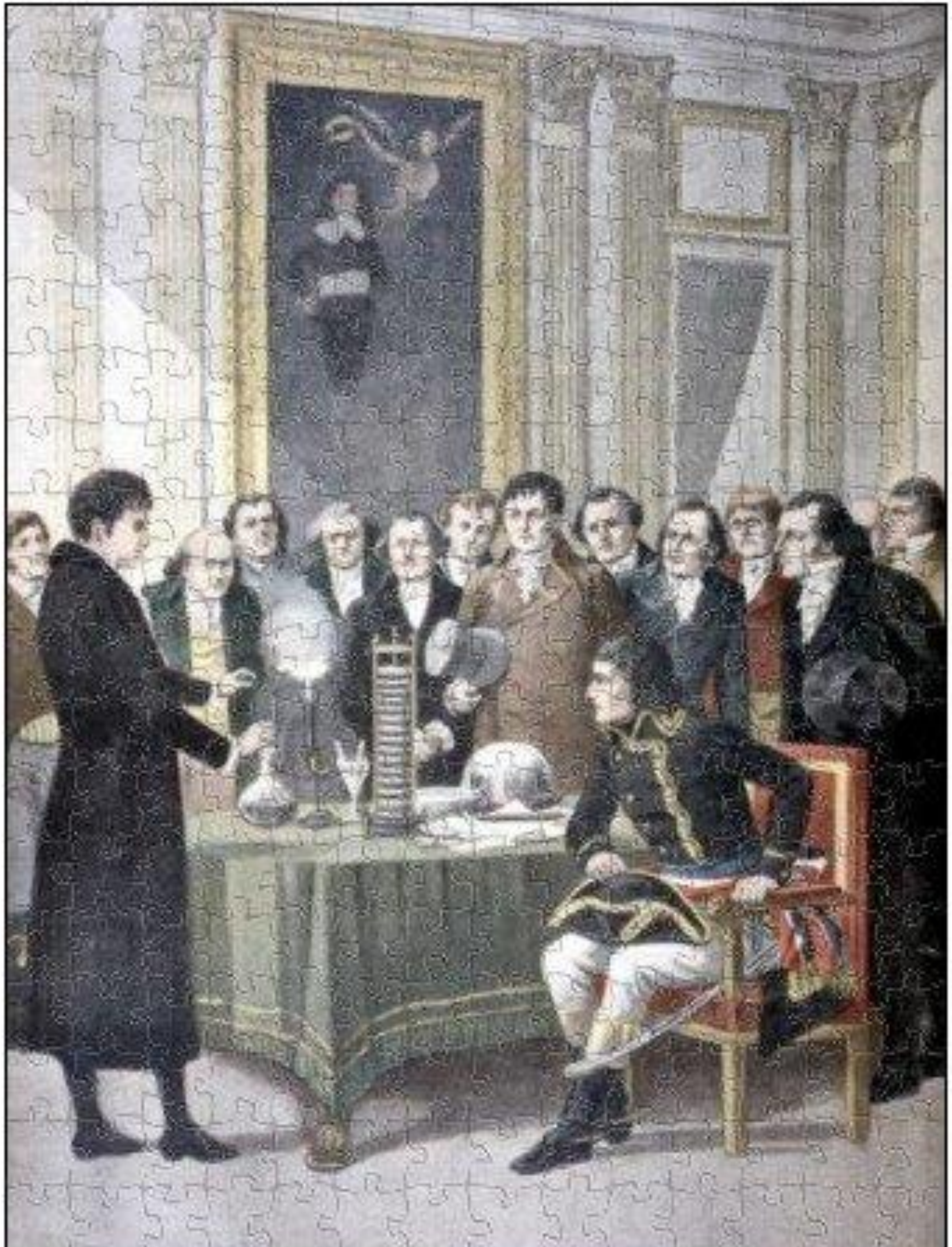
POWERFUL HEAT

How to increase efficiency of thermopower generation and refrigeration?

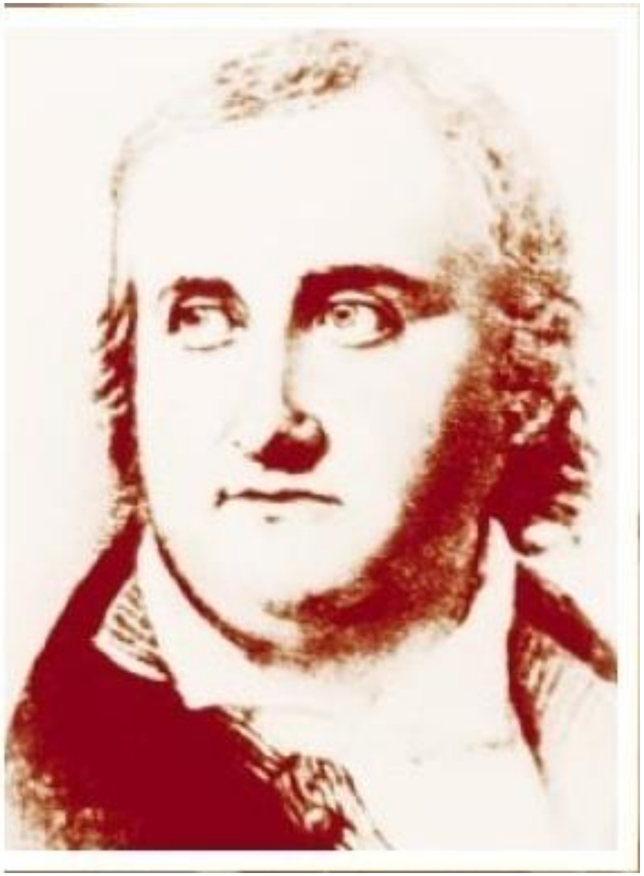
A dynamical systems approach

A.Volta (Como)

Volta effect: **an electric potential difference is developed by the contact of two different metals at the same temperature.**



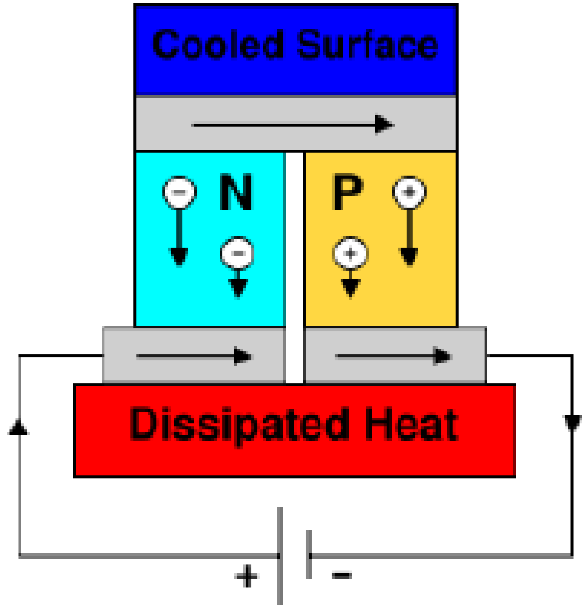
A.Volta (Como)

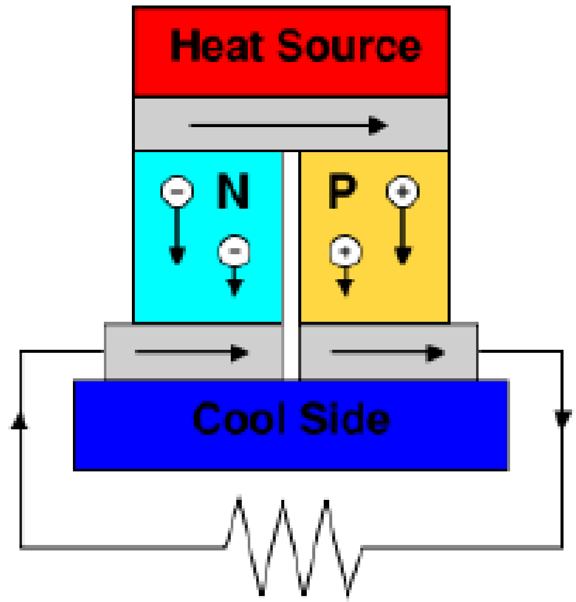


Seebeck

In 1822, the Estonian–German physicist Thomas Johann Seebeck discovered that if heat is applied across the junction of two wires, a current is generated.

Thermoelectricity concerns the conversion of temperatures differencies into electrical potential or viceversa





It can be used to perform useful electrical work or to pump heat from cold to hot place, thus performing refrigeration

Abram Ioffe, 1950s :
doped semiconductors have large thermoelectric effect

The initial excitement about semiconductors in 1950 was due to their promise, not in electronics but in refrigeration. The discovery that semiconductors can act as efficient heat pumps led to expectations of environmentally benign solid state home refrigerators and power generators

Oil burning lamp powering a radio using the first commercial thermoelectric generator containing ZnSb and constantan built in USSR beginning in 1948

During this 1960–1995 period, the thermoelectric field received little attention from the worldwide scientific research community.

Nevertheless, the thermoelectric industry grew slowly and steadily, by finding niche applications:

space missions
laboratory equipment
medical applications

where cost and energy efficiency were not as important as energy availability, reliability, predictability, and the quiet operation of equipment.

Thermoelectric devices provide on board power to operate radio signal trasmitters, on board computers, gyros and navigational systems, spectrometers and many other scientific instruments.

These power generating systems can operate unattended, maintenance free, for many years

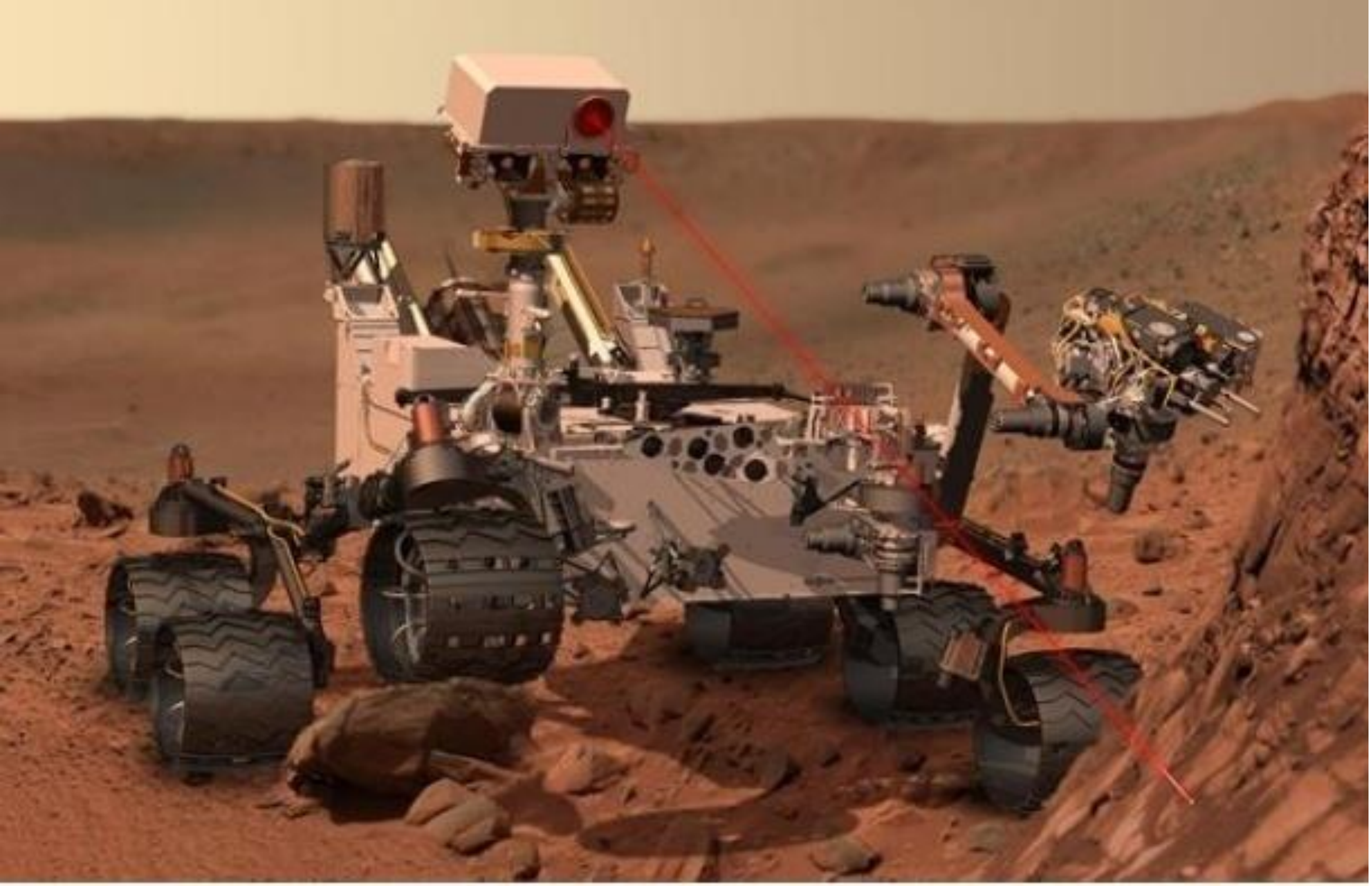
NASA uses thermoelectric because key advantages include high reliability, small size and no noise.

New Horizon spacecraft to Pluto

(The RTG is the black, cylindrical finned object at lower left).

Radioisotope Thermoelectric Generators (RTGs) is the only technology (so far) capable of providing electrical power for deep-space missions including:

- Voyagers I and II,
- Galileo, Cassini, and the New Horizons mission to Pluto



MARS SCIENCE LABORATORY -Robotic space probe- **august 2012**

Curiosity Rover **is powered by a radioisotope thermoelectric Generator (5kg Plutonium-238)**


BioLite

USS DOLPHIN AGSS 555
–
Test for Silent Running

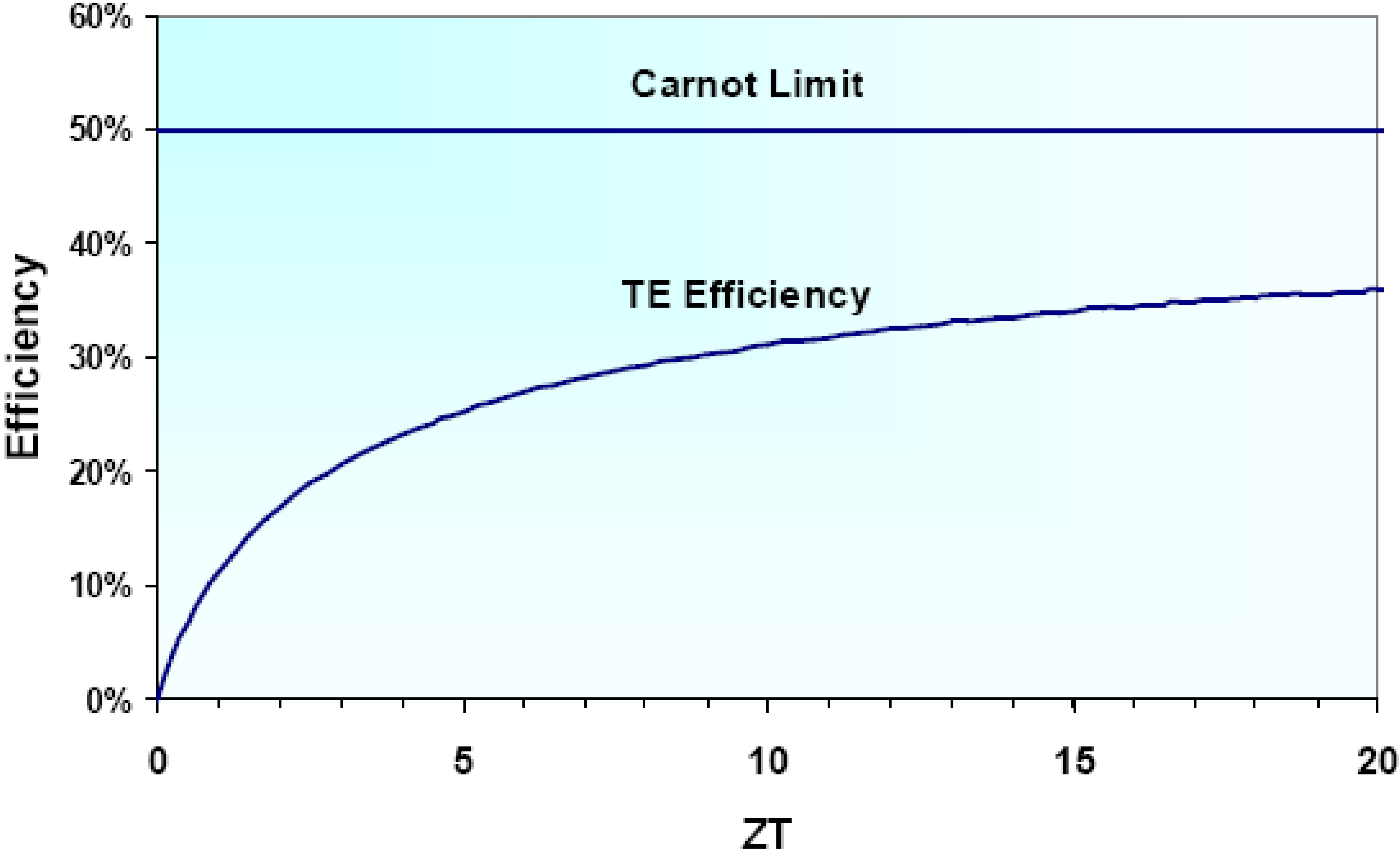
The suitability of a thermoelectric material for energy conversion or electronic refrigeration is evaluated by

The ZT figure of merit

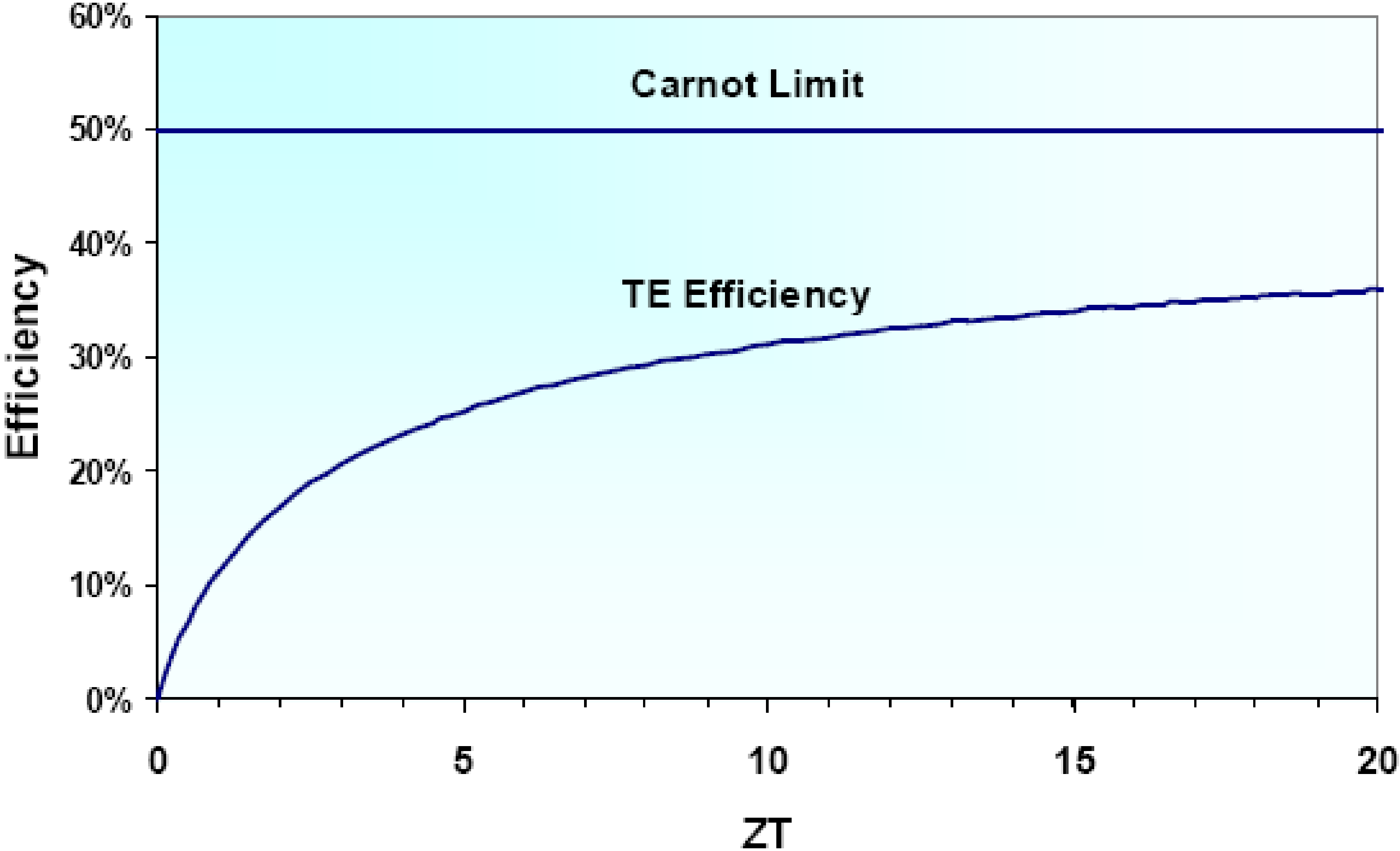
The suitability of a thermoelectric material for energy conversion or electronic refrigeration is evaluated by

In linear response regime:

and for time-reversal symmetric systems



Best thermoelectric material have ZT around 1



Best thermoelectric material have ZT around 1

A ZT value > 3 would make solid –state home refrigerators <u>economically competitive</u> with compressor-based refrigerators

$$J_u = L_{uu}\,\partial_x\left(\frac{1}{T}\right) + L_{u\varrho}\,\partial_x\left(-\frac{\mu}{T}\right)$$

$$J_\varrho = L_{\varrho u}\,\partial_x\left(\frac{1}{T}\right) + L_{\varrho\varrho}\,\partial_x\left(-\frac{\mu}{T}\right)$$

$$J_u = L_{uu}\,\partial_x\left(\frac{1}{T}\right) + L_{u\varrho}\,\partial_x\left(-\frac{\mu}{T}\right)$$

$$J_\varrho = L_{\varrho u}\,\partial_x\left(\frac{1}{T}\right) + L_{\varrho\varrho}\,\partial_x\left(-\frac{\mu}{T}\right)$$

$$\sigma = \frac{e^2}{T} L_{\varrho\varrho}$$

$$\kappa = \frac{1}{T^2}\frac{\det \mathbb{L}}{L_{\varrho\varrho}}$$

$$S = \frac{1}{eT}\left(\frac{L_{u\varrho}}{L_{\varrho\varrho}} - \mu\right)$$

$$J_u = L_{uu}\,\partial_x\left(\frac{1}{T}\right) + L_{u\varrho}\,\partial_x\left(-\frac{\mu}{T}\right)$$

$$J_\varrho = L_{\varrho u}\,\partial_x\left(\frac{1}{T}\right) + L_{\varrho\varrho}\,\partial_x\left(-\frac{\mu}{T}\right)$$

$$\sigma = \frac{e^2}{T} L_{\varrho\varrho} \qquad \kappa = \frac{1}{T^2}\frac{\det \mathbb{L}}{L_{\varrho\varrho}}$$

$$S = \frac{1}{eT}\left(\frac{L_{u\varrho}}{L_{\varrho\varrho}} - \mu\right)$$

$$ZT = \frac{\left(L_{u\varrho} - \mu L_{\varrho\varrho}\right)^2}{\det \mathbb{L}} \qquad = \frac{\sigma S^2}{\kappa} T$$

$$J_u = L_{uu}\,\partial_x\left(\frac{1}{T}\right) + L_{u\varrho}\,\partial_x\left(-\frac{\mu}{T}\right)$$

$$J_\varrho = L_{\varrho u}\,\partial_x\left(\frac{1}{T}\right) + L_{\varrho\varrho}\,\partial_x\left(-\frac{\mu}{T}\right)$$

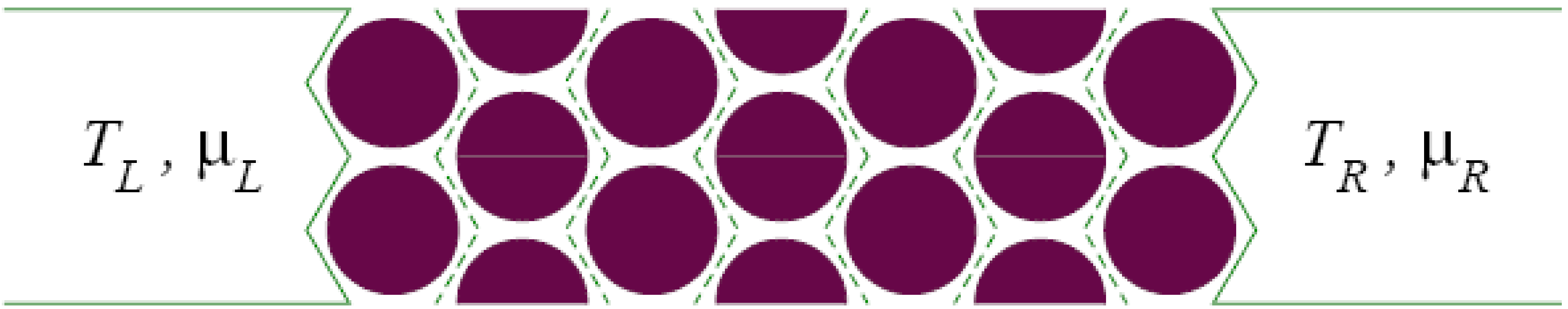
Thermodynamics restrictions:

$$\det \mathbf{L} \geq 0 \qquad L_{uu} \geq 0 \qquad L_{\rho\rho} \geq 0$$

$$L_{u\rho} = L_{\rho u}$$

$$\boxed{ZT \geq 0}$$

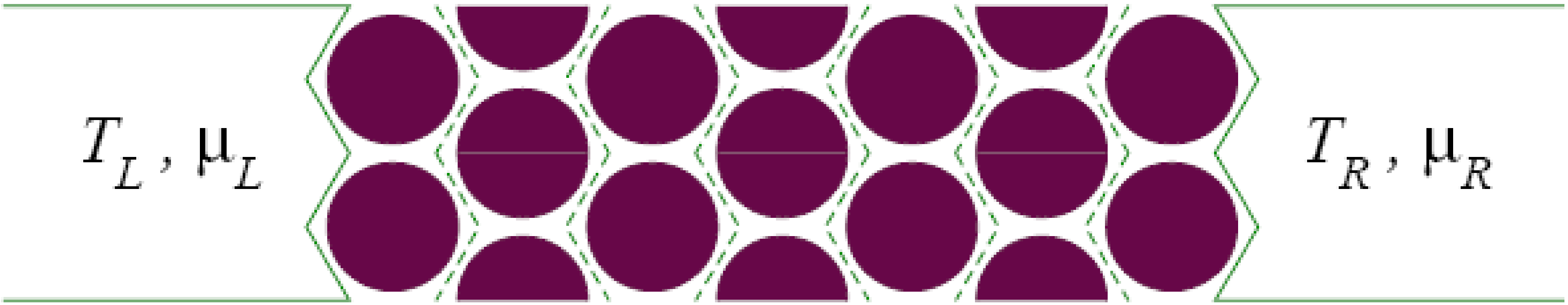
Consider a two dimensional gas with circular scatterers (Lorentz gas model)



$$\mu = T \ln \left(\frac{c_D \, \gamma}{T^{(D+1)/2}} \right) \qquad \gamma = \frac{\lambda}{(2\pi m)^{1/2}} \varrho T^{1/2}$$

Consider a two dimensional gas with circular scatterers (Lorentz gas model)

ZT =1.5

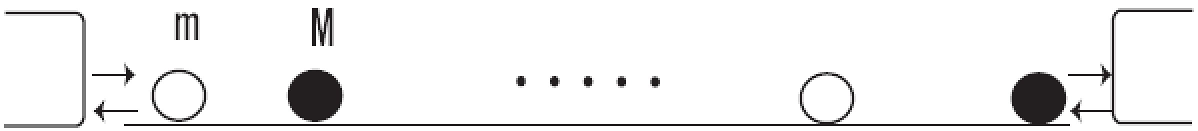


$$\mu = T \ln\left(\frac{c_D\,\gamma}{T^{(D+1)/2}}\right) \qquad \gamma = \frac{\lambda}{(2\pi m)^{1/2}}\varrho T^{1/2}$$

Interacting system

Consider a one dimensional gas of elastically interacting particles with unequal masses:

m M

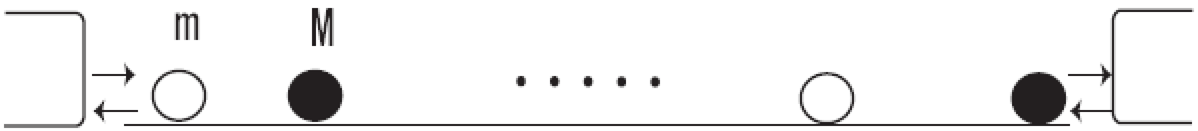


G.C. , Lei Wang, T. Prosen: J. of Stat. Mech. (2009)

Interacting system

Consider a one dimensional gas of elastically interacting particles with unequal masses:

m M



For the equal mass case m=M, the system is integrable and ZT=1

G.C. , Lei Wang, T. Prosen: J. of Stat. Mech. (2009)

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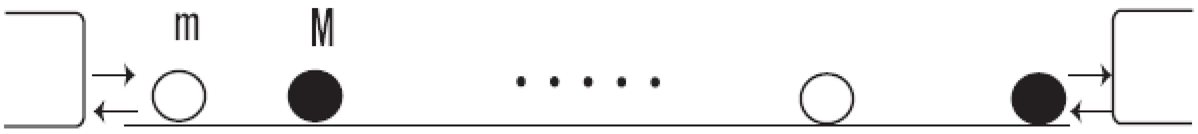

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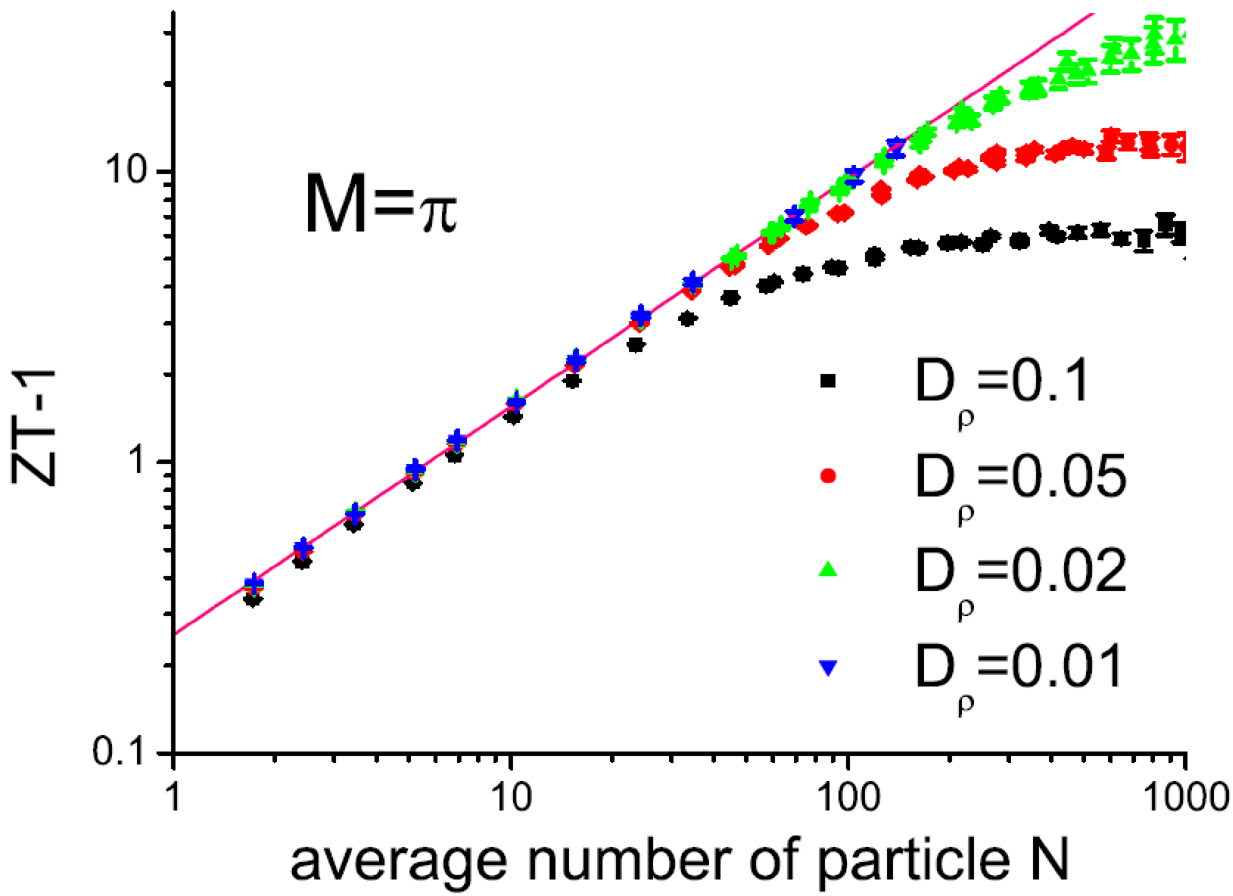
G.C. , Lei Wang, T. Prosen: J. of Stat. Mech. (2009)

G.C. , Lei Wang, T. Prosen: J. of Stat. Mech. (2009)

ZT diverges with increasing number of particles



CONSERVATION LAWS

Suzuki formula: (generalizes Mazur inequality)

For a system of finite size Λ

$$C_{ij}(\Lambda) \equiv \lim_{t\to\infty} \frac{1}{t} \int_0^t dt' \langle J_i(t') J_j(0) \rangle_T$$

$$= \sum_{n=1}^{M} \frac{\langle J_i Q_n \rangle_T \langle J_j Q_n \rangle_T}{\langle Q_n^2 \rangle_T}$$

The sum is extended over all the M relevant Q_n (non orthogonal to the flows) constants of motion

G. Benenti, G.C., Wang Jiao: prl (2013)

Then the finite size generalized Drude weight

$$D_{ij}(\Lambda) \equiv \frac{1}{2\Lambda} C_{ij}(\Lambda)$$

is different from zero

If at the thermodynamic limit:

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

and

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

then the transport is balistic

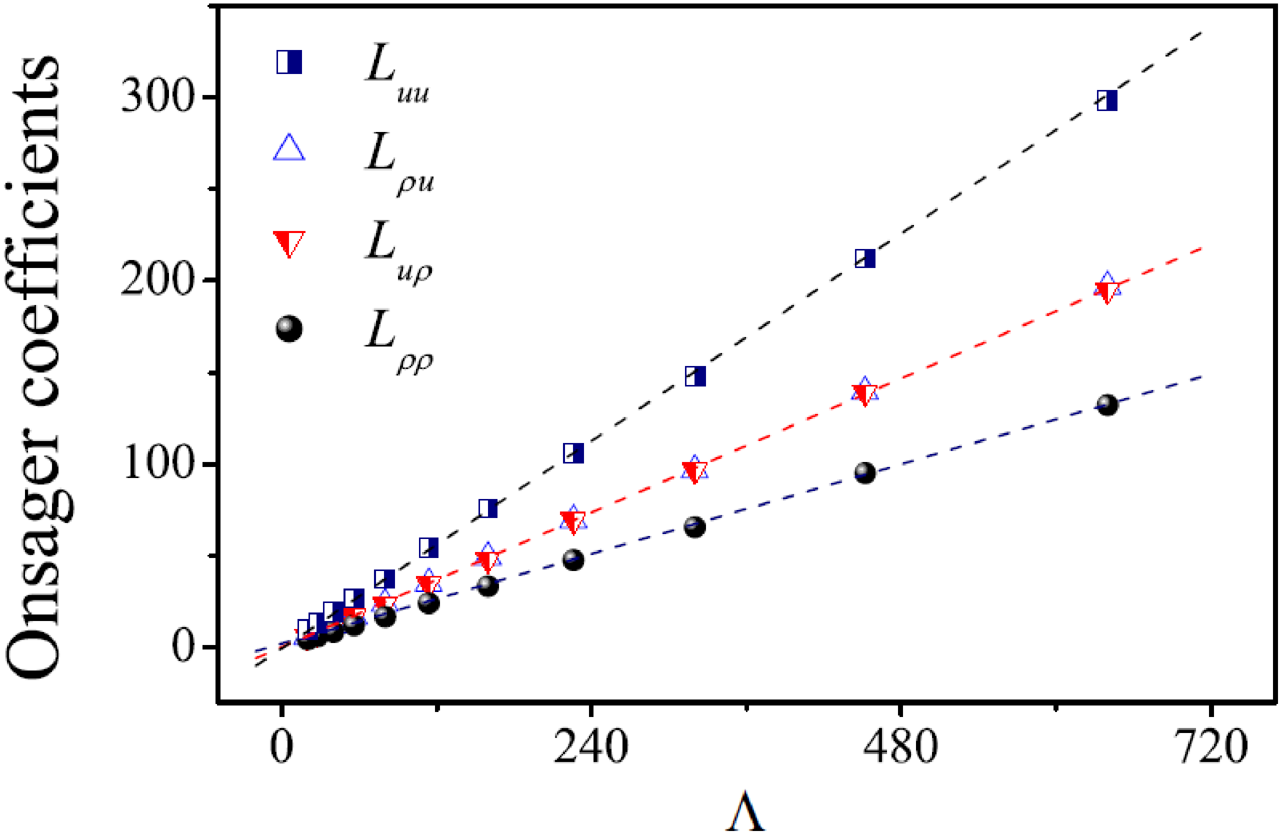
Total momentum is conserved: $P = \sum_{i=1}^{N} m_i v_i$

$$\boxed{Q_1 = P}$$

Total momentum is conserved: $P = \sum_{i=1}^{N} m_i v_i$

$$Q_1 = P$$

Non-equilibrium computations for the 1D gas



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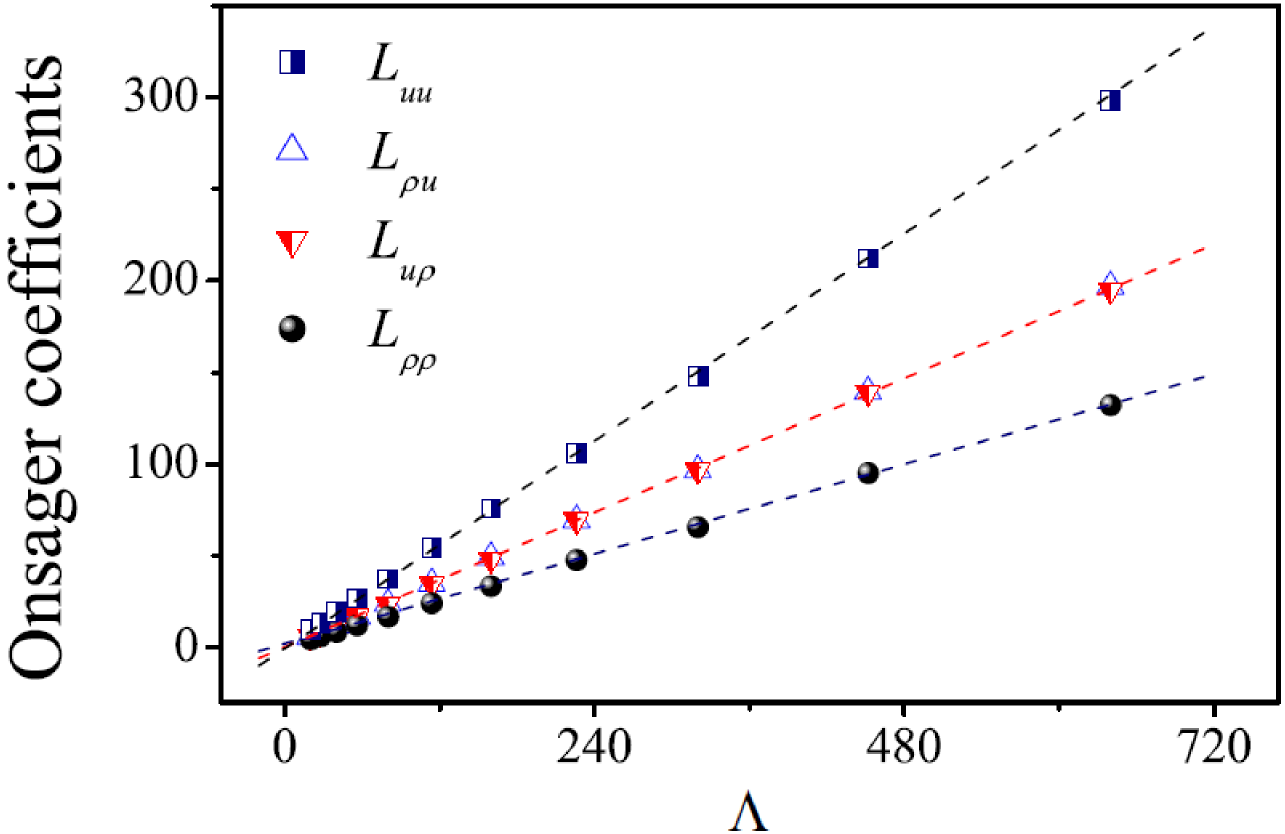

$$\sigma = \frac{L_{\rho\rho}}{T},$$

Total momentum is conserved: $P = \sum_{i=1}^{N} m_i v_i$

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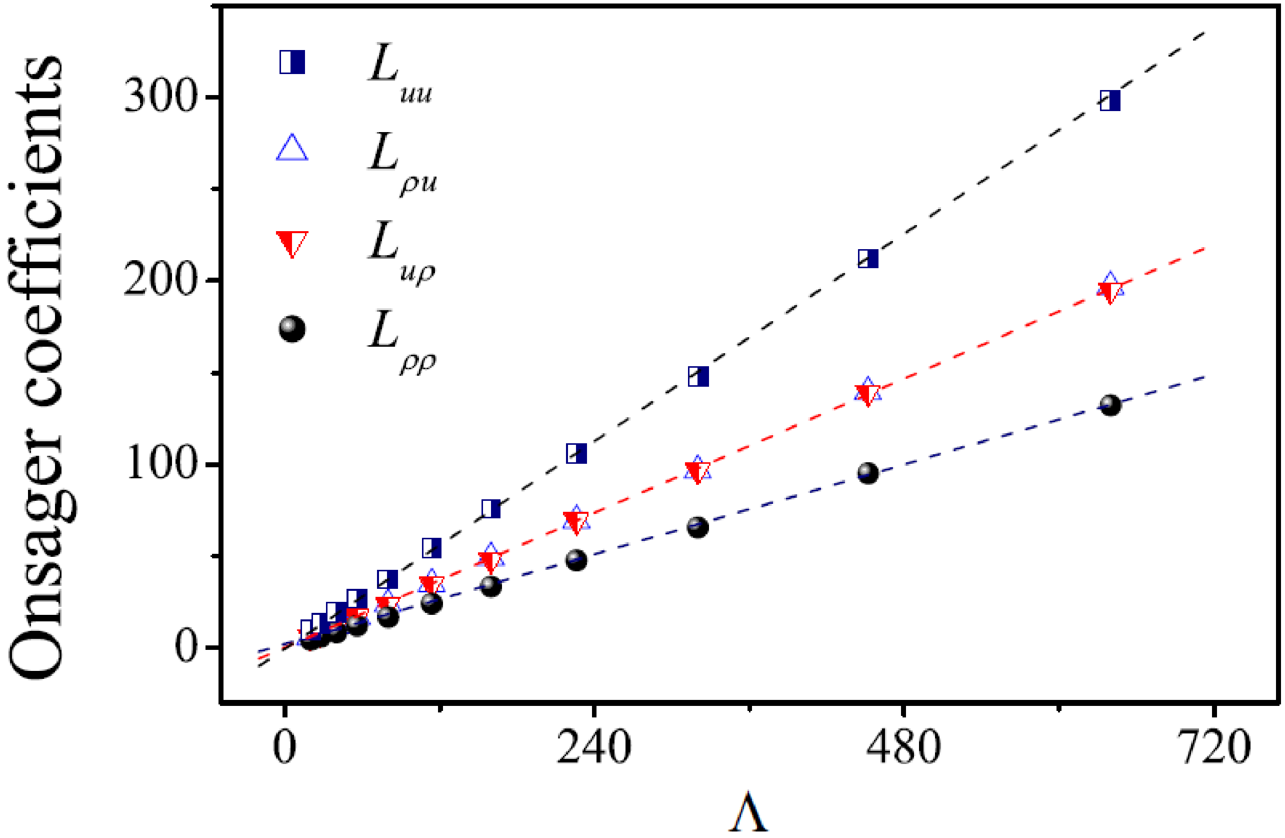
Non-equilibrium computations for the 1D gas



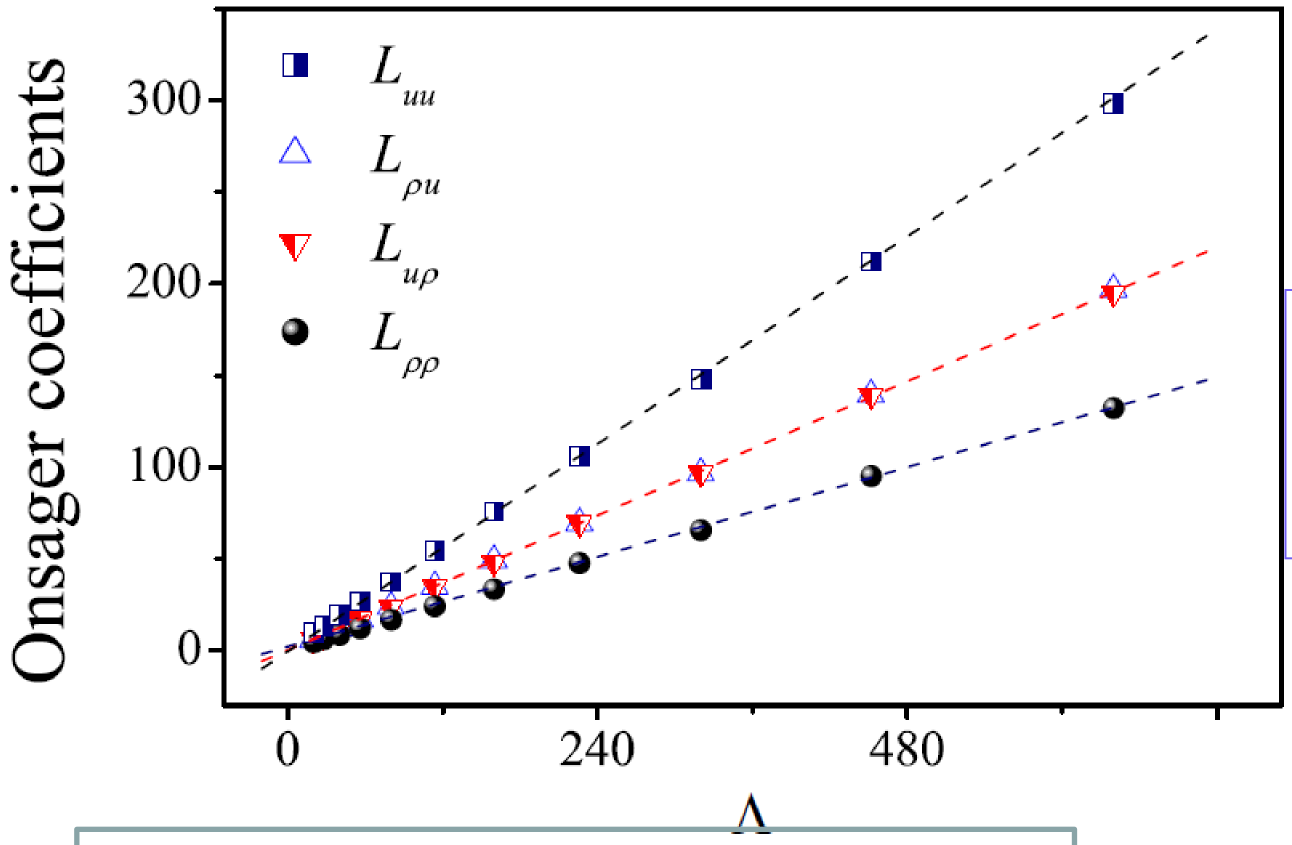
$$\sigma = \frac{L_{\rho\rho}}{T},$$

$$S = L_{\rho u}/T L_{\rho\rho} \propto \Lambda^0$$

Total momentum is conserved: $P = \sum_{i=1}^{N} m_i v_i$

$$Q_1 = P$$

Non-equilibrium computations for the 1D gas



$$\sigma = \frac{L_{\rho\rho}}{T};$$

$$\kappa = \frac{1}{T^2}\frac{\det \mathbb{L}}{L_{\varrho\varrho}}$$

$$S = L_{\rho u}/T L_{\rho\rho} \propto \Lambda^0$$

If there is a single, relevant, constant of motion, M=1 due to Suzuki formula:

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

The ballistic contribution to det L vanishes thus implying that det L increases slower than Λ^2

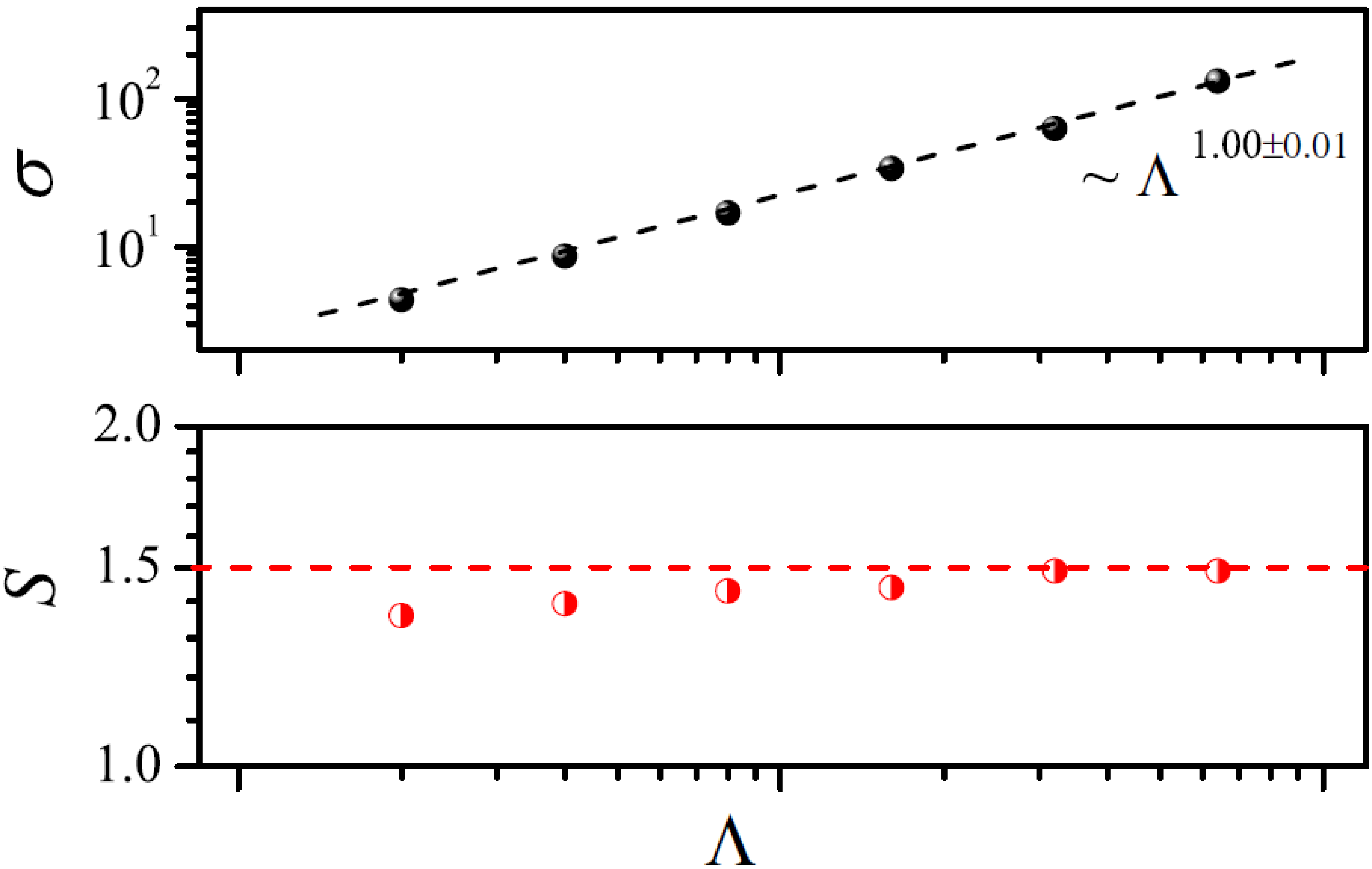
Then $\kappa \propto \det L / L_{\rho\rho} \propto \Lambda^{\alpha}, \text{with } \alpha < 1$

(sub-ballistic)

$$ZT = \sigma S^2 T / \kappa \propto \Lambda^{1-\alpha}$$

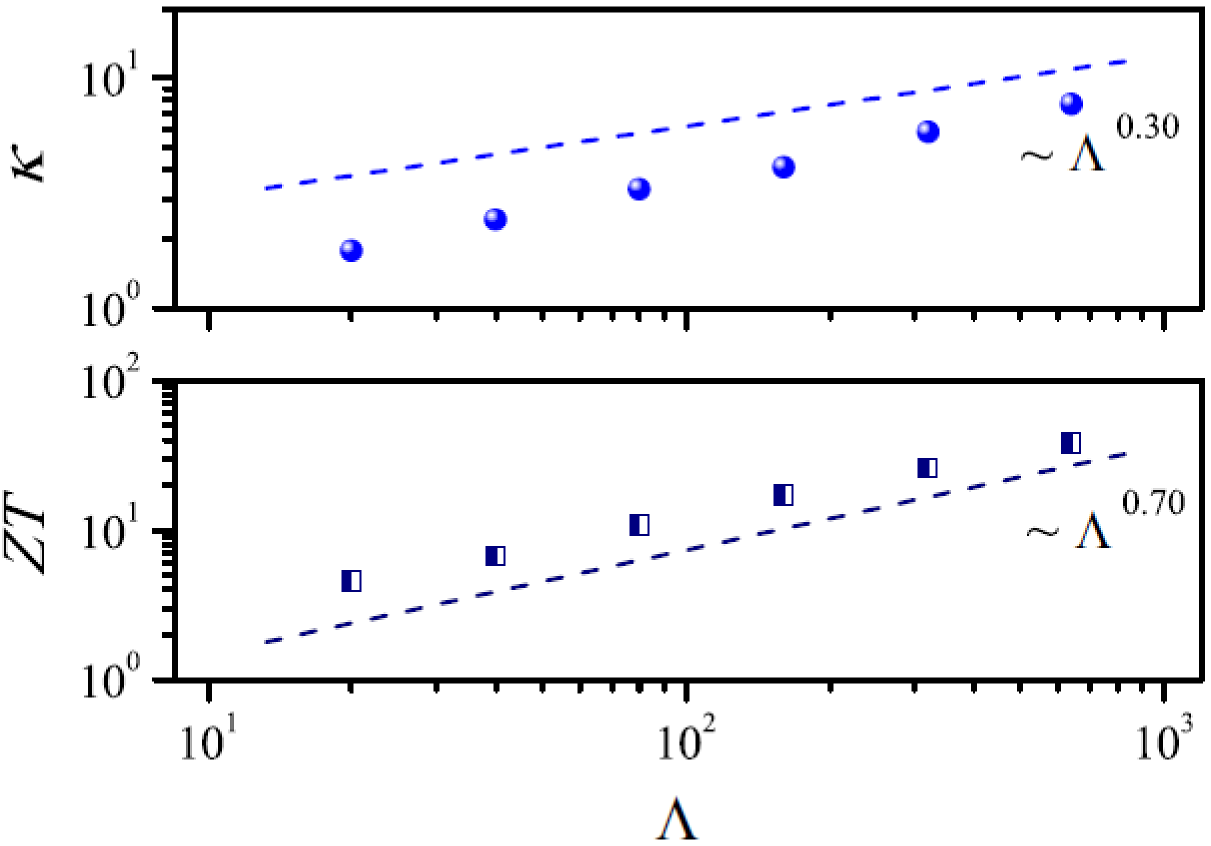
ZT diverges in the thermodynamic limit

Non-equilibrium computations for the 1D gas



G. Benenti, G.C., Wang Jiao: prl (2013)

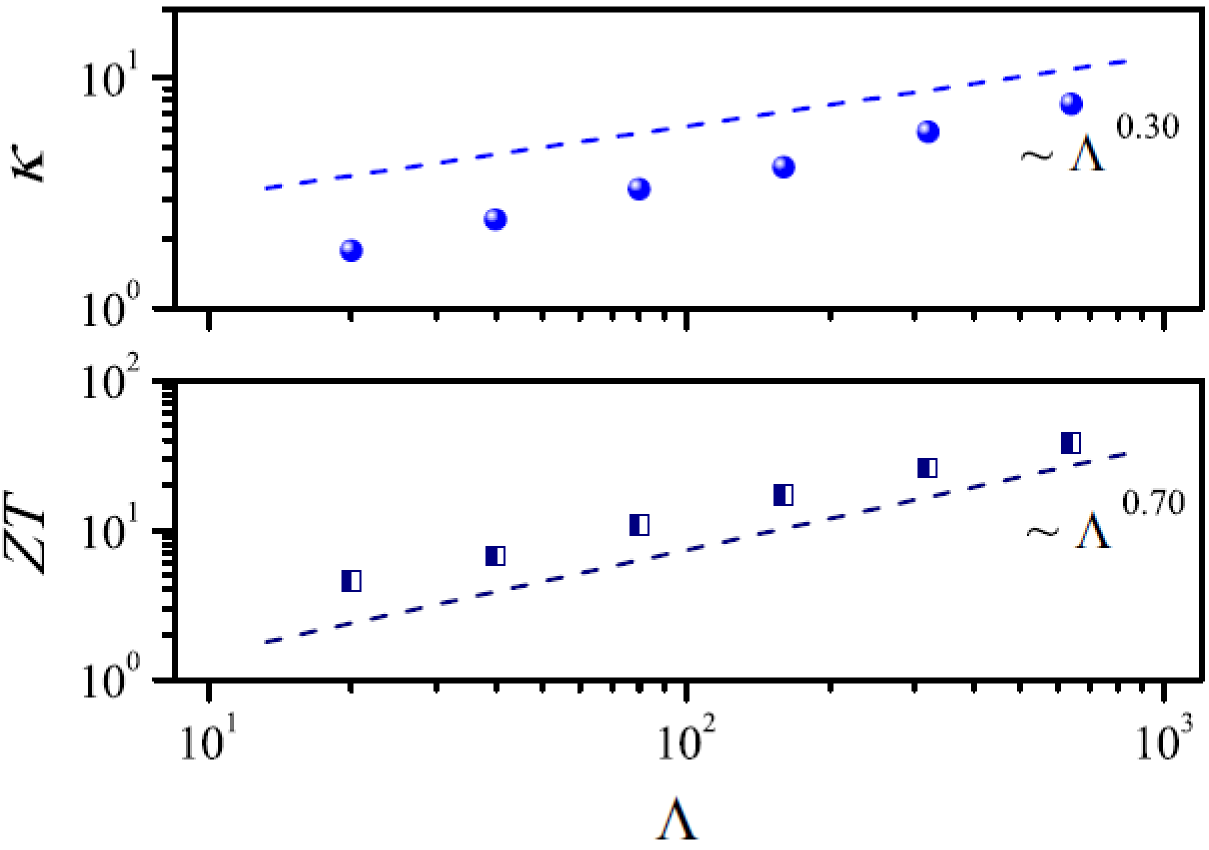
Non-equilibrium computations



ZT diverges

G. Benenti, G.C., Wang Jiao: prl (2013)

Non-equilibrium computations

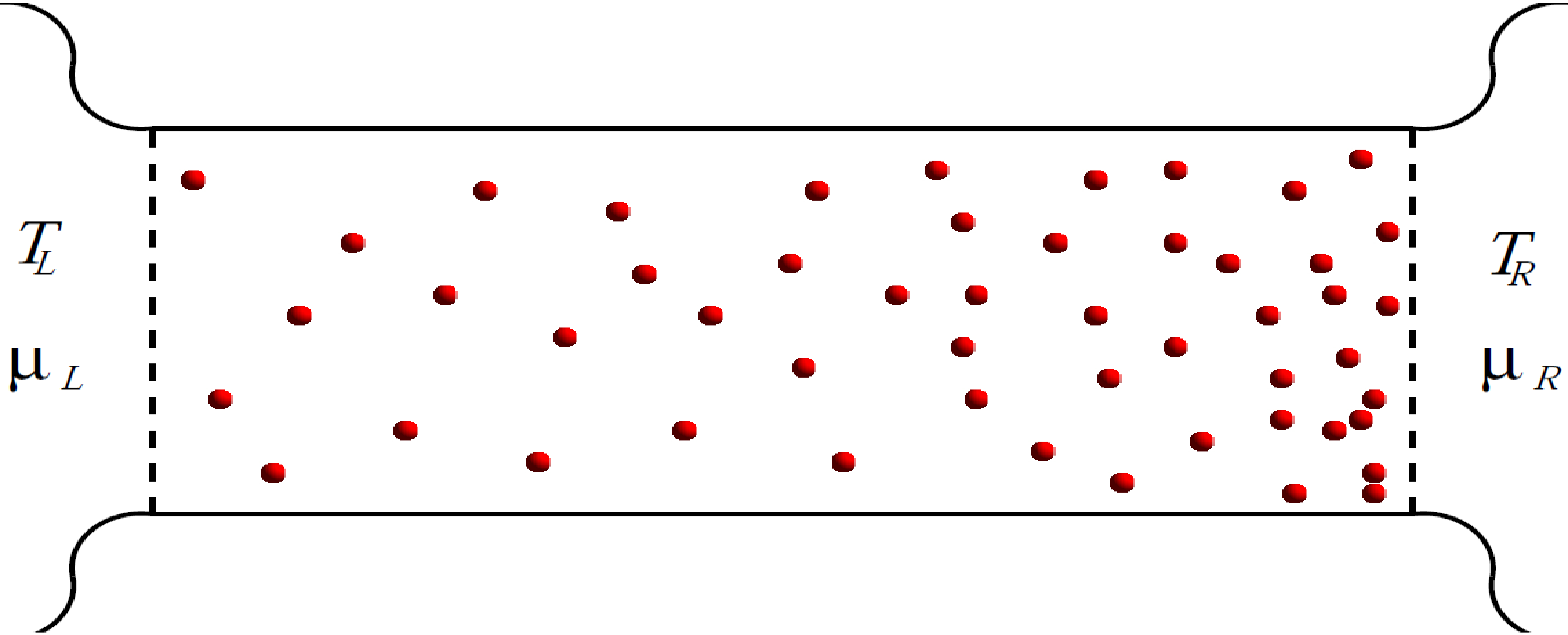


ZT diverges

G. Benenti, G.C., Wang Jiao: prl (2013)

In the integrable case (M=1) ZT=1

MULTIPARTICLE COLLISION DYNAMICS



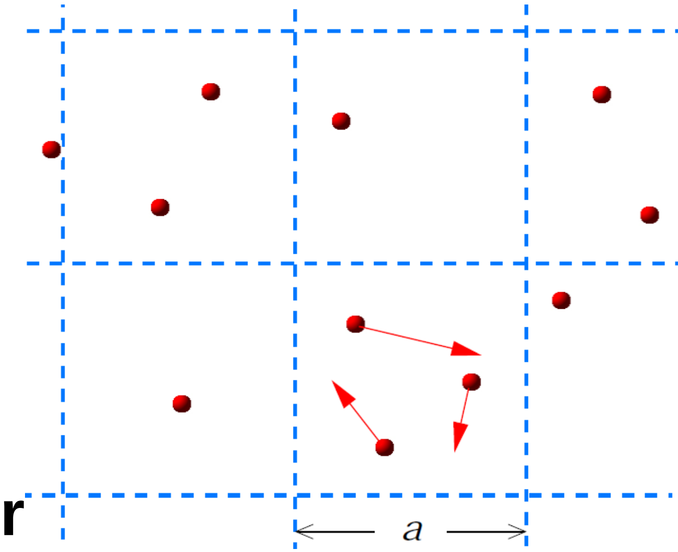
$$\gamma_k = \frac{w}{(2\pi m)^{1/2}} \rho_k T_k^{1/2}$$

$$\mu_k = T_k \ln\left(\frac{\gamma_k}{T_k^{3/2}}\right) + \mu_0$$

The system evolves in discrete time steps τ :

Free propagation: $\vec{r}_i \longrightarrow \vec{r}_i + \vec{v}_i \tau$

Collision:



-divide the volume in identical cells of linear size a

-the velocities of particles in the same cell are rotated with respect to the center of mass velocity by a random angle

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

$$\vec{V}_{\mathrm{CM}} = \frac{1}{\mathcal{N}} \sum_{i=1}^{\mathcal{N}} \vec{v}_i$$

Collision preserves total energy and total momentum

The time interval τ between collisions and the collision angle α tune the strength of interaction and affect transport coefficients.

If α multiple of 2π no interaction

If $\alpha = \pi/2$ most efficient mixing

Our simulations:. $n = N/lw = 22.75$

$l = 500 \quad w = 2$

$\alpha = \pi/2$ $\tau = 0.25$ $a = 0.1$

Particle current $$J_\rho = \sum_{i=1}^{N} v_{x,i}$$

Energy current $$J_u = \frac{1}{2} m \sum_{i=1}^{N} \left(v_{x,i}^2 + v_{y,i}^2\right) v_{x,i}$$

Constant of motion $$Q_1 = p_x = m \sum_{i=1}^{N} v_{x,i}$$

From Suzuki formula:

$$C_{\rho\rho}(l) = \frac{NT}{m}$$

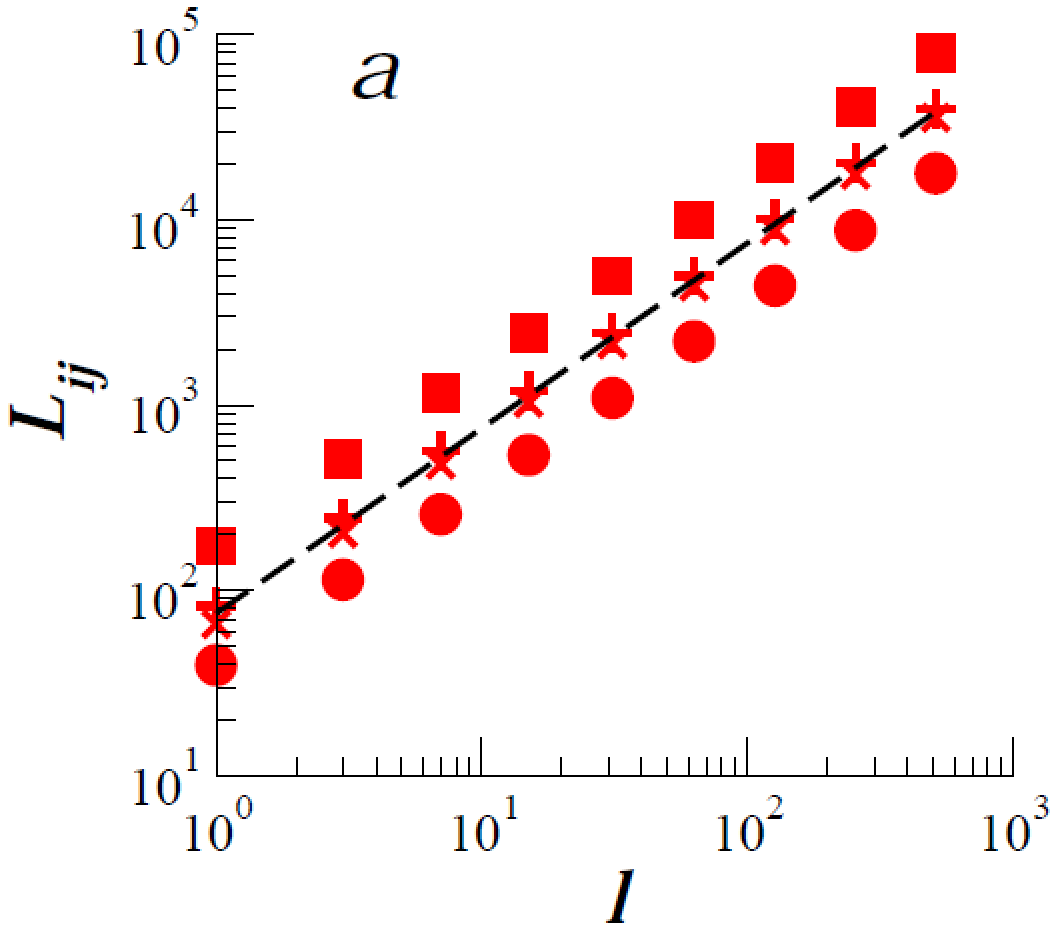
$$C_{\rho u}(l) = \frac{2NT^2}{m}$$

$$C_{uu}(l) = \frac{4NT^3}{m}$$

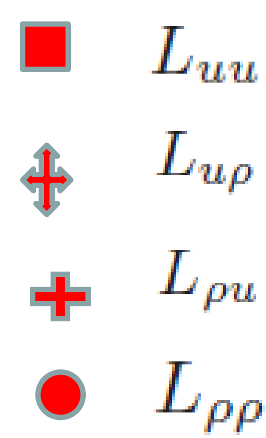
$$D_{ij}(l) \equiv \frac{1}{2\Omega(l)} C_{ij}(l) \qquad N \propto \Omega(l) = lw$$

The Drude weigths do not scale with l: ⇨ **the transport is ballistic:**

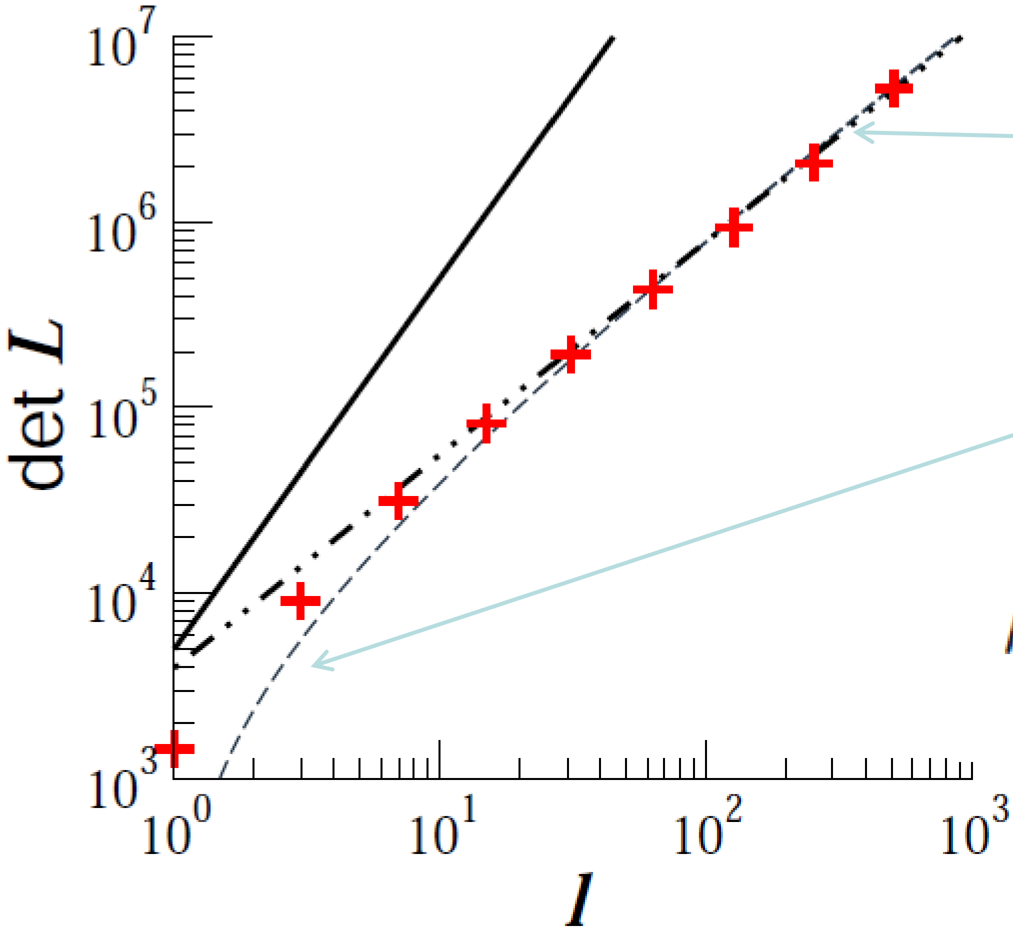
$$L_{ij} \sim l.$$



Non equilibrium simulations



The ballistic contribution to det (L) is zero since: $\mathcal{D}_{\rho\rho}\mathcal{D}_{uu} - \mathcal{D}^2_{\rho u} = 0$



$$\det(\boldsymbol{L}) \approx l^{1.15}$$

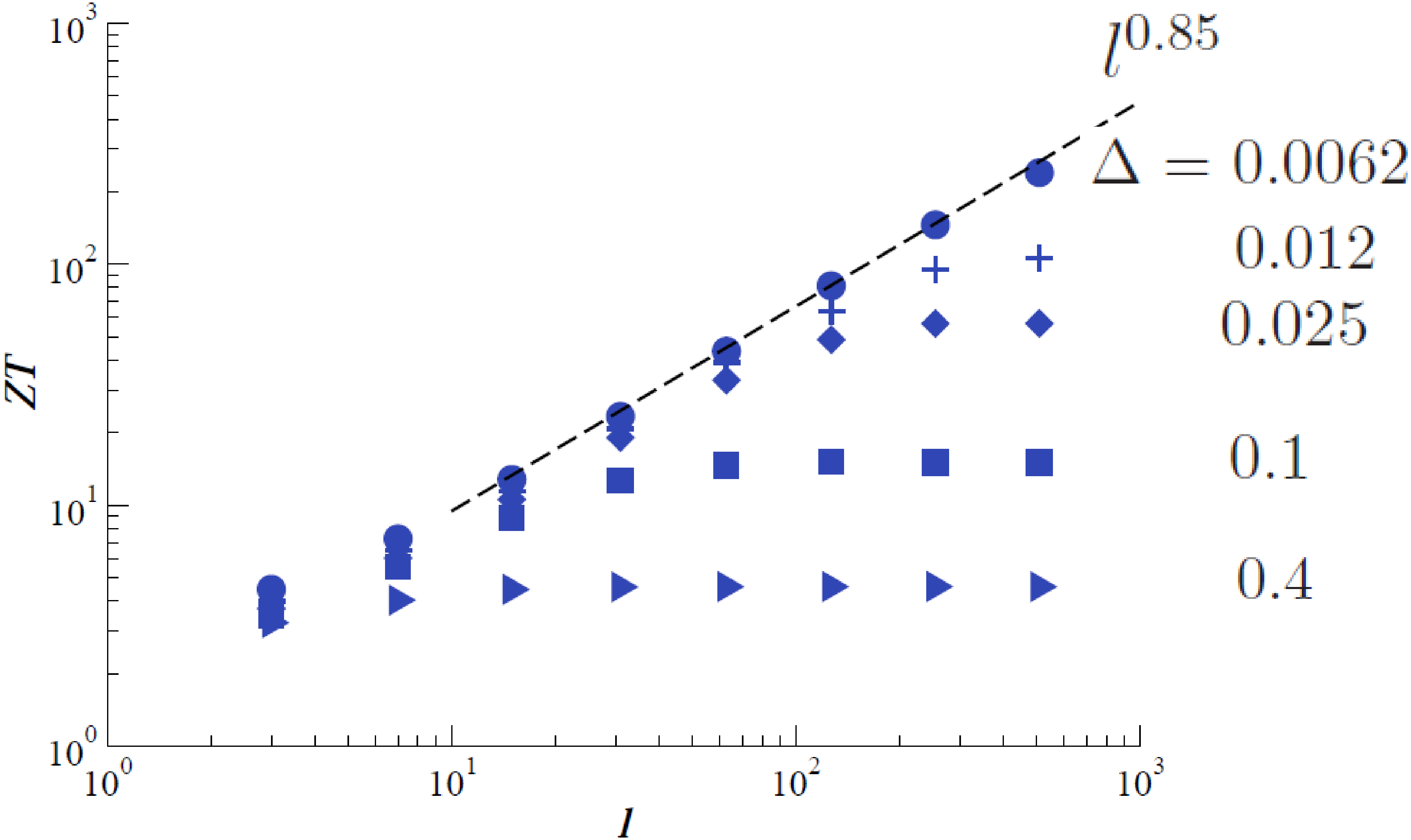
$$\det(\boldsymbol{L}) \sim l \log(l)$$

$$\kappa = \frac{1}{T^2} \frac{\det \boldsymbol{L}}{L_{\rho\rho}} \sim \log(l)$$

Mode coupling theory and hydrodynamics predicts logarithmic divergence of thermal conductivity K

ZT greatly enhanced by the single conserved quantity

$$Q_1 = p_x = m \sum_{i=1}^{N} v_{x,i}$$



Stability of enhancement of ZT

In real systems total momentum is never conserved due to phonon field, presence of impurities or inelastic scattering events

Introduce **stochastic noise**:

after a collision, the particles in a cell are reflected $\vec{v}_i \to -\vec{v}_i$
with probability

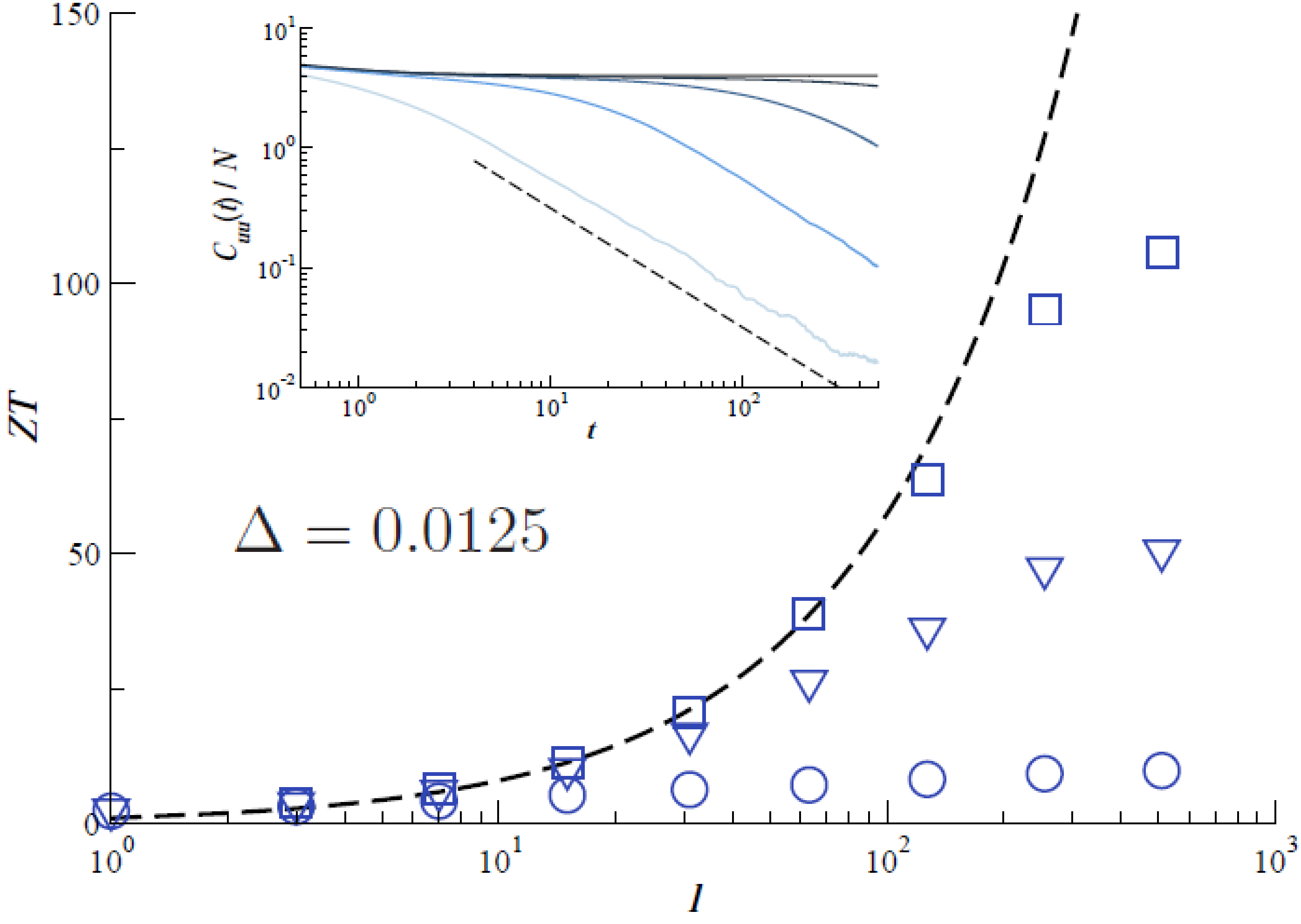
For any total momentum is not conserved

If is small, momentum conservation is only weakly broken

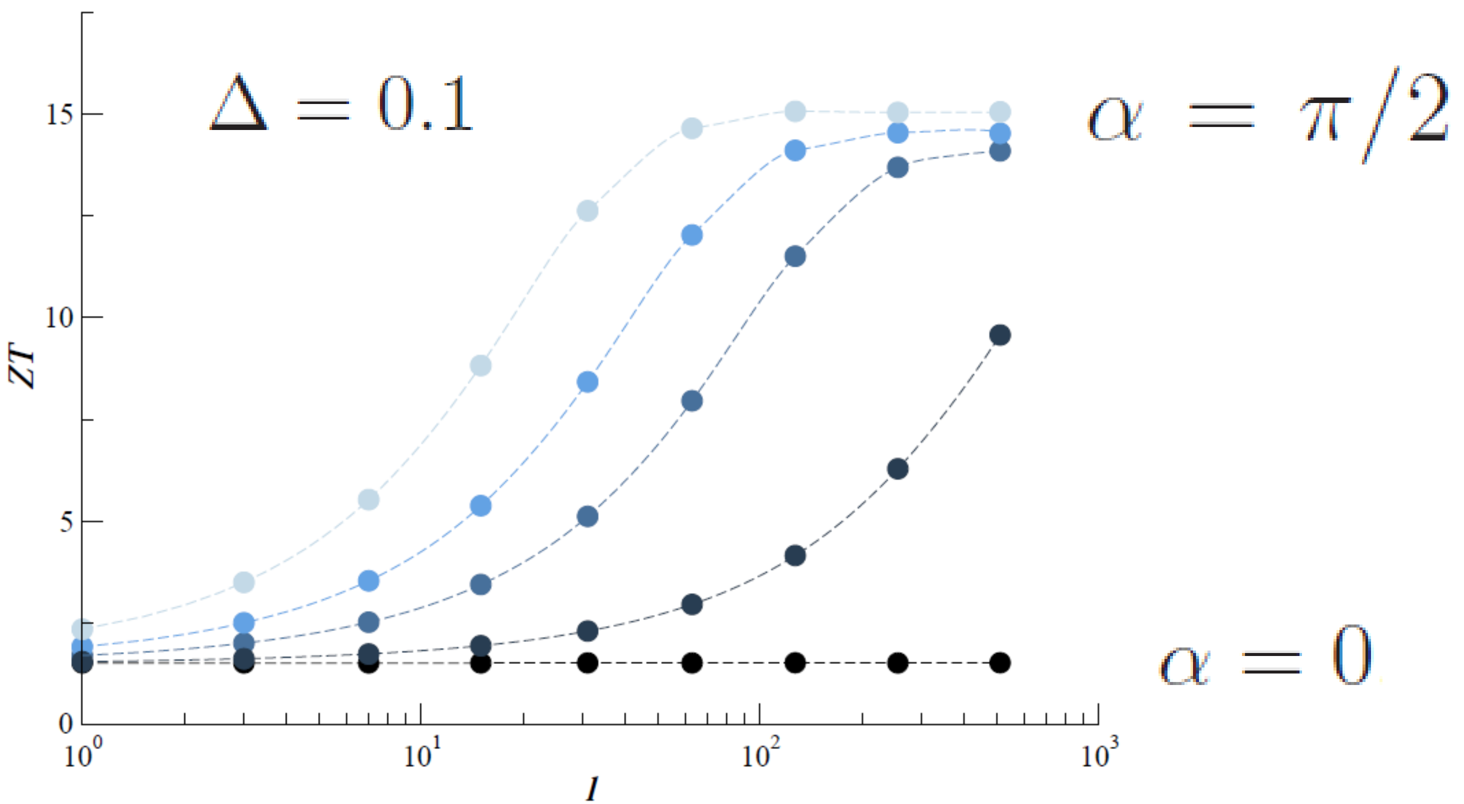
EFFECT OF STOCHASTIC NOISE

The absence of conserved quantities, M=0, leads to correlations decay and zero Drude coefficients

ZT becomes size independent



In the non interacing limit $\alpha = 0$ the momentum of each particle is conserved: $M \propto l$ → **ZT=3/2**



ZT=3/2

A new challenge:

Break time-reversal symmetry

A new challenge:
Break time-reversal symmetry

$$\sigma(\boldsymbol{B}) = \frac{e^2}{T} L_{\rho\rho}(\boldsymbol{B})$$

$$\kappa(\boldsymbol{B}) = \frac{1}{T^2} \frac{\det \boldsymbol{L}(\boldsymbol{B})}{L_{\rho\rho}(\boldsymbol{B})}$$

$$S(\boldsymbol{B}) = \frac{L_{\rho q}(\boldsymbol{B})}{eTL_{\rho\rho}(\boldsymbol{B})}$$

$$S(-\boldsymbol{B}) = \frac{L_{q\rho}(\boldsymbol{B})}{eTL_{\rho\rho}(\boldsymbol{B})}$$

Onsager- Casimir

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

A new challenge:
Break time-reversal symmetry

$$\sigma(\boldsymbol{B}) = \frac{e^2}{T} L_{\rho\rho}(\boldsymbol{B}) \qquad \kappa(\boldsymbol{B}) = \frac{1}{T^2} \frac{\det \boldsymbol{L}(\boldsymbol{B})}{L_{\rho\rho}(\boldsymbol{B})}$$

$$S(\boldsymbol{B}) = \frac{L_{\rho q}(\boldsymbol{B})}{eTL_{\rho\rho}(\boldsymbol{B})} \qquad S(-\boldsymbol{B}) = \frac{L_{q\rho}(\boldsymbol{B})}{eTL_{\rho\rho}(\boldsymbol{B})}$$

Onsager- Casimir

$$L_{ij}(\boldsymbol{B}) = L_{ji}(-\boldsymbol{B}) \quad \Longrightarrow \quad \begin{array}{l} \sigma(\boldsymbol{B}) = \sigma(-\boldsymbol{B}) \\ \kappa(\boldsymbol{B}) = \kappa(-\boldsymbol{B}) \end{array}$$

however $$S(\boldsymbol{B}) \neq S(-\boldsymbol{B})$$

G. Benenti, K. Saito and G.C. prl 106 230602 (2011)

Maximum efficiency and efficiency at maximun power depend on two parameters x and y

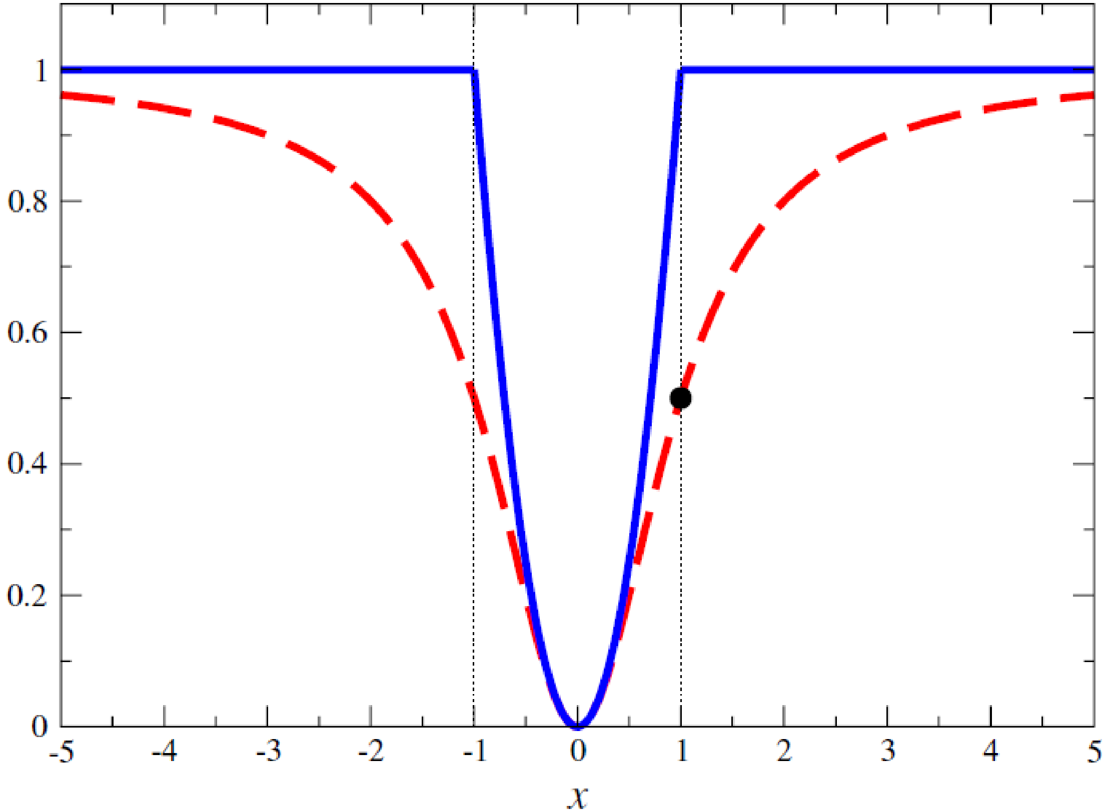
$$x \equiv \frac{L_{\rho q}}{L_{q\rho}} = \frac{S(\boldsymbol{B})}{S(-\boldsymbol{B})}$$

(x=1 implies y=ZT)

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

The second, asymmetry parameter, x offers an additional freedom for efficiency of thermoelectric devices

Maximum efficiency



Efficiency at maximum power

G. Benenti, K. Saito and G.C. prl 106 230602 (2011)

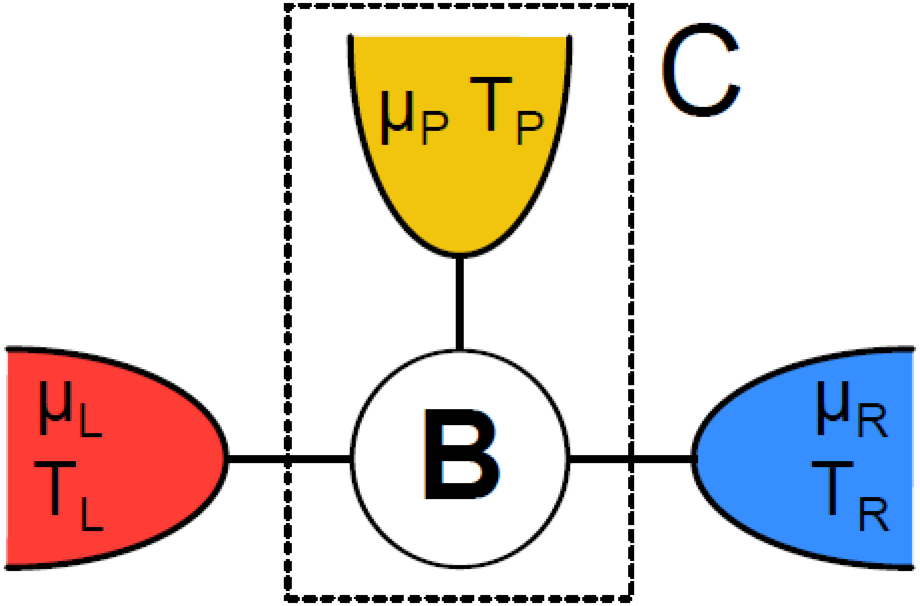
For non interacting systems $S(B) = S(-B)$

due to symmetry properties of the scattering matrix

Inelastic scattering introduced e.g. by a, selfconsistent, third terminal, leads to non-symmetric thermopower

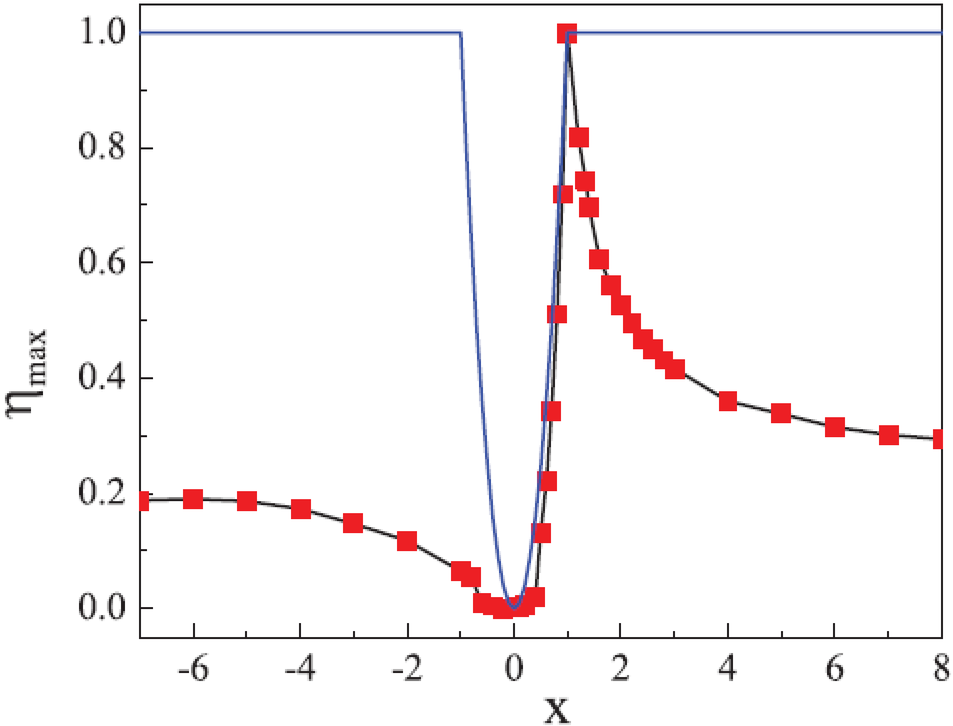
K. Saito, G. Benenti, G.C., T. Prosen PRB 84 201306 (2011)

Temperature and chemical potential of the third reservoir are chosen, self-consistently that is no net exchange of particles and heat occurs.



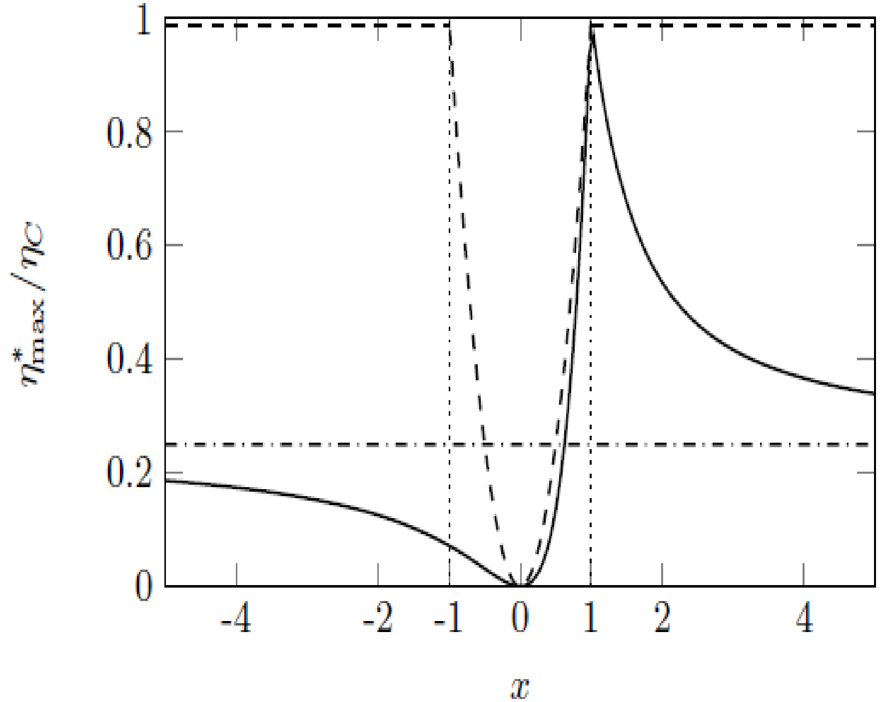
originally proposed by Buttiker have become a common tool to simulate inelastic events in an otherwise conservative system

Maximum efficiency

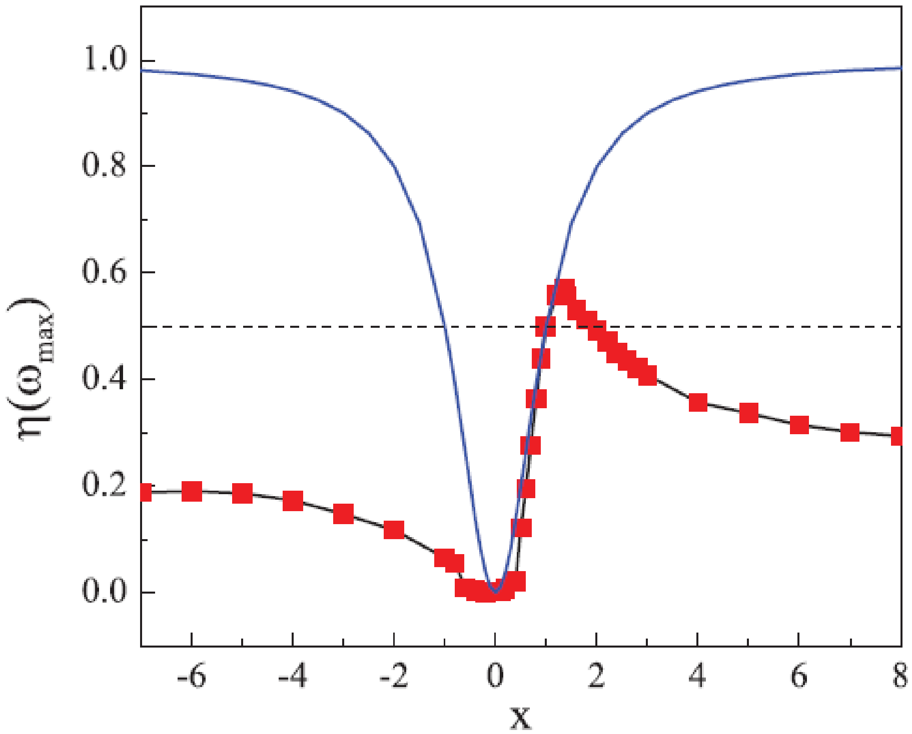


V. Balachandran, G. Benenti, G.C., PRB 87, 165419 (2013)

Limitation imposed by Unitarity of the scattering matrix



K. Brandner, K.Saito, U. Seifert, prl (2013)

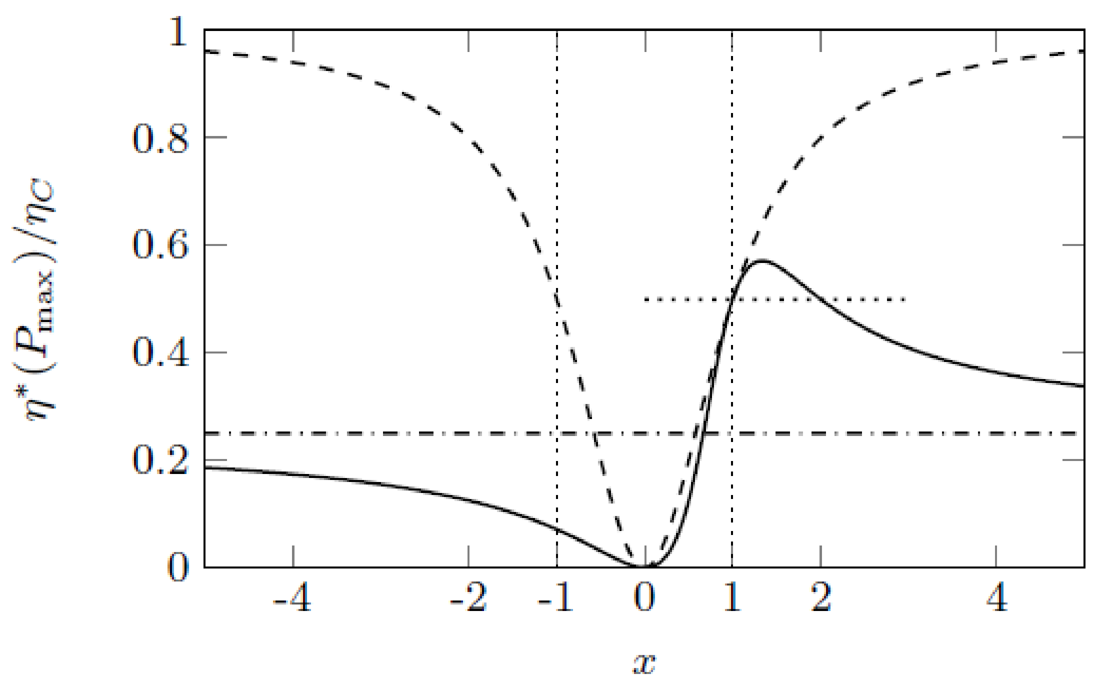


Efficiency at maximum power

Curzon-Ahlborn limit

V. Balachandran, G. Benenti, G.C., PRB 87, 165419 (2013)

Limitation imposed by Unitarity of the scattering matrix



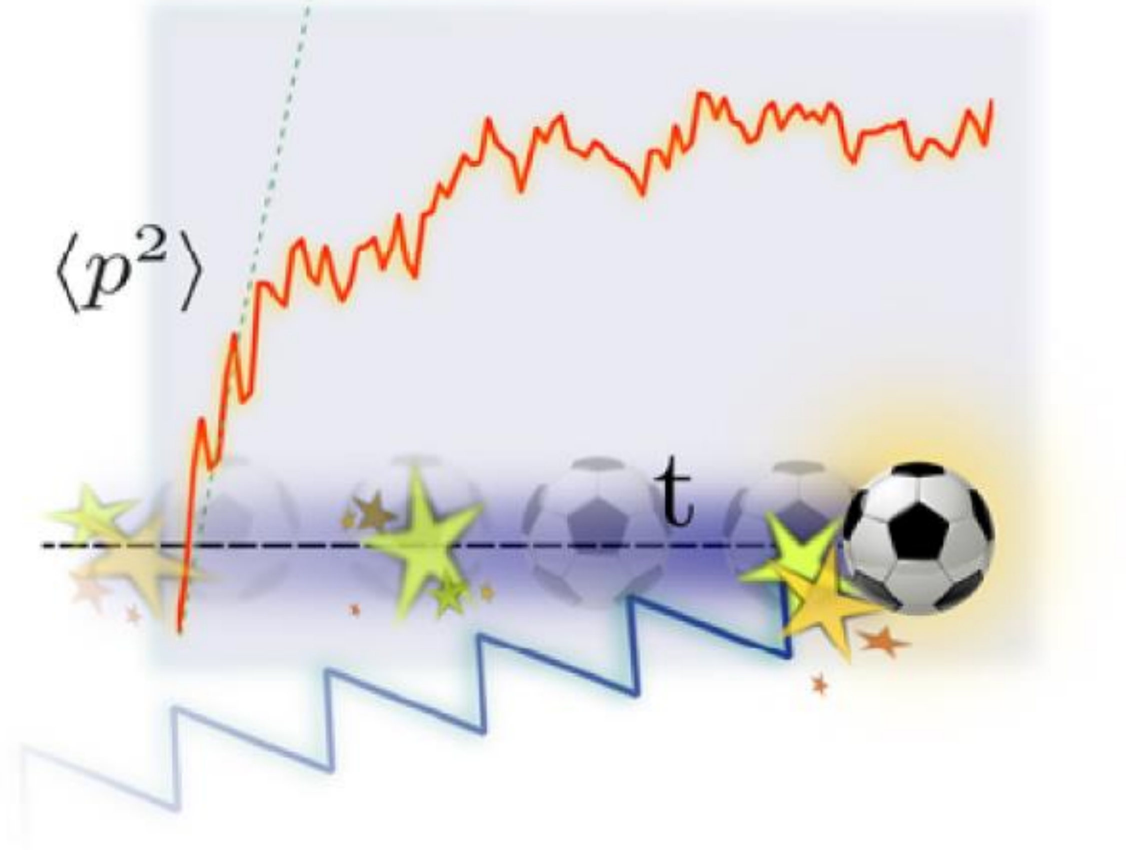
K. Brandner, K.Saito, U. Seifert, prl (2013)

Thermal diodes and wave diodes

Phys Rev Lett 88 094302 (2002)
Phys Rev Lett. 93 184301 (2004)
Chaos 15 015120 (2005)
Phys Rev Lett 98 104302 (2007)
Phys Rev Lett 106 164101 (2011)
Phys Rev E 86 010101 (2012)

Thermoelectric

Phys Rev Lett 101 01601 (2008)
J Stat Mech L03004 (2009)
Phys Rev E 80 010102 (2009)
Phys Rev E 80 031136 (2009)
Chem. Phys. 375, 508 (2010)
Phil. Trans. R. Soc.A 369, 466 (2011)
J Stat Mech P10026 (2011)
Phys Rev B 84 201306 (2011)
Phys Rev Lett 106 230602 (2011)
Phys Rev E 86 052102 (2012)
Phys Rev Lett 110, 070604 (2013)
Phys Rev B 87, 165419 (2013)
New J. Phys 16, 015014 (2014)
Arxiv 1311.4430



Features thought to be unique to quantum dynamical systems, such as localization of momentum, are found in a classical kicked rotor - where particles move in a ring and a 'kicked' periodically by an external field that changes the particle's momentum.

Italo Guarneri, Giulio Casati, and Volker Karle
Phys. Rev. Lett. **113**, 174101 (2014) (/prl/abstract/10.1103/PhysRevLett.113.174101)

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

Benenti, Casati, Prosen, Saito :"Fundamental aspects of steady state heat to work conversion"
cond-mat arXiv:1311.4430

The Green-Kubo formula expresses the Onsager coefficients in terms of correlation functions of the corresponding current operators

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

$$L_{ij}(\omega) = \lim_{\epsilon \to 0} \int_0^\infty dt e^{-i(\omega - i\epsilon)t}$$

$$\times \lim_{\Lambda \to \infty} \frac{1}{\Lambda} \int_0^\beta d\tau \langle J_i J_j (t + i\tau) \rangle_T$$

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

unitarity of the scattering matrix as
a general physical principle imposes a strong restriction
on the Onsager coefficients that lead to a significant reduction reduction
of the attainable efficiency of any thermoelectric
device within the broad and well-established class of
three-terminal models

Asymmetric power generation and refrigeration

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

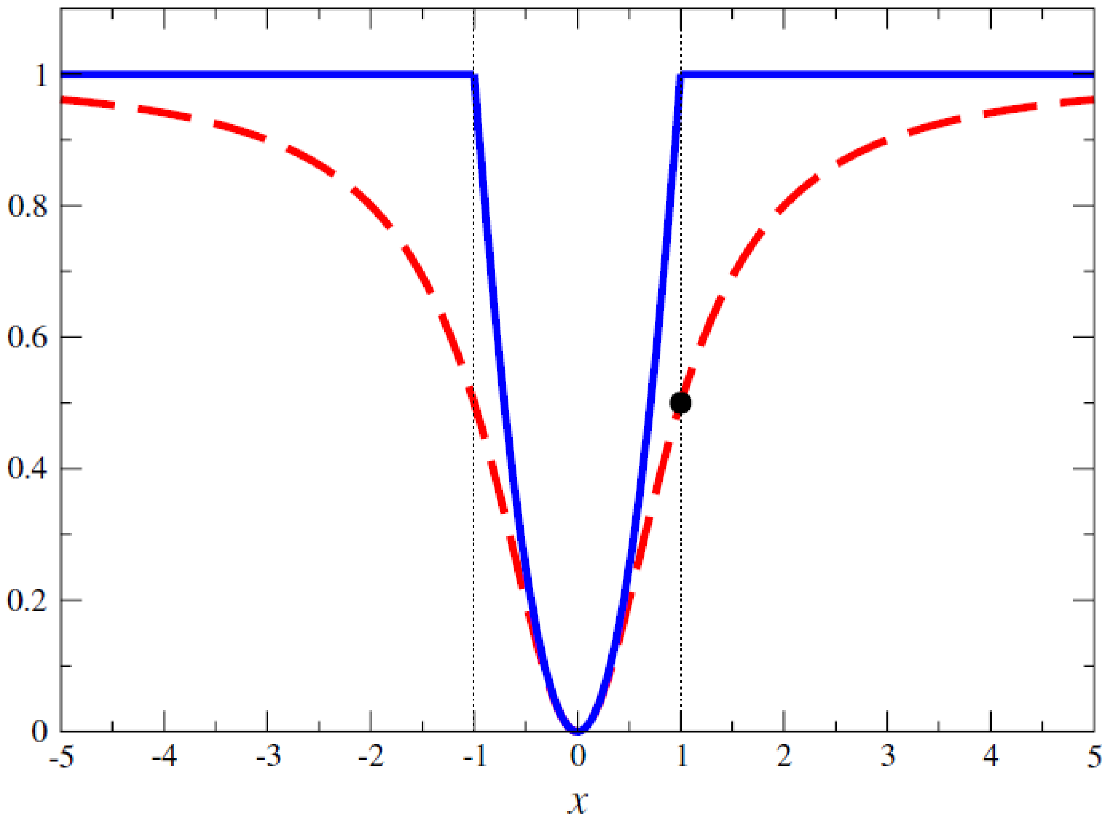
$$\eta_{\max} = \eta_C \, x \, \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1}, \qquad \eta_{\max}^{(r)} = \eta_C \, \frac{1}{x} \, \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1}$$

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

Maximum efficiency



efficiency at maximum

power

Efficiency at maximum power

G. Benenti, K. Saito and G.C. prl 106 230602 (2011)

$$J_\rho = \sum_i v_i$$ **Particles current**

$$J_u = \sum_i \frac{1}{2} m_i v_i^3$$ **Energy current**

$$J_m \equiv \sum_{i=1}^N m_i v_i$$ **mass current = P**

(conserved quantity)

$$J_m \sim \bar{m} J_\rho$$

We expect that also the particles current does not decay

$$\sigma \sim \Lambda$$

Asymmetric power generation and refrigeration

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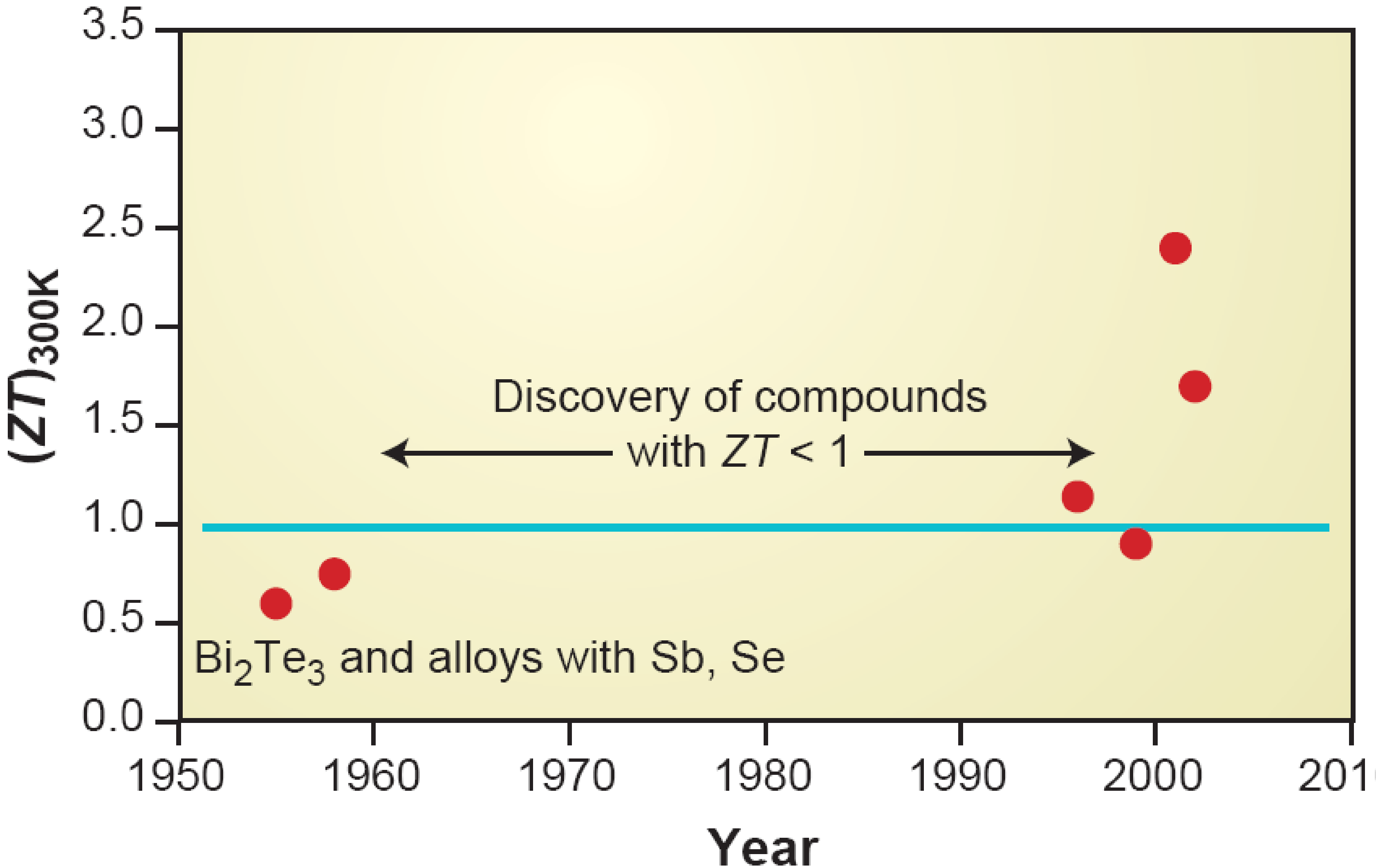
A ZT value > 3 would make solid –state home refrigerators economically competitive with compressor-based refrigerators

A ZT value > 3 would make solid –state home refrigerators economically competitive with compressor-based refrigerators

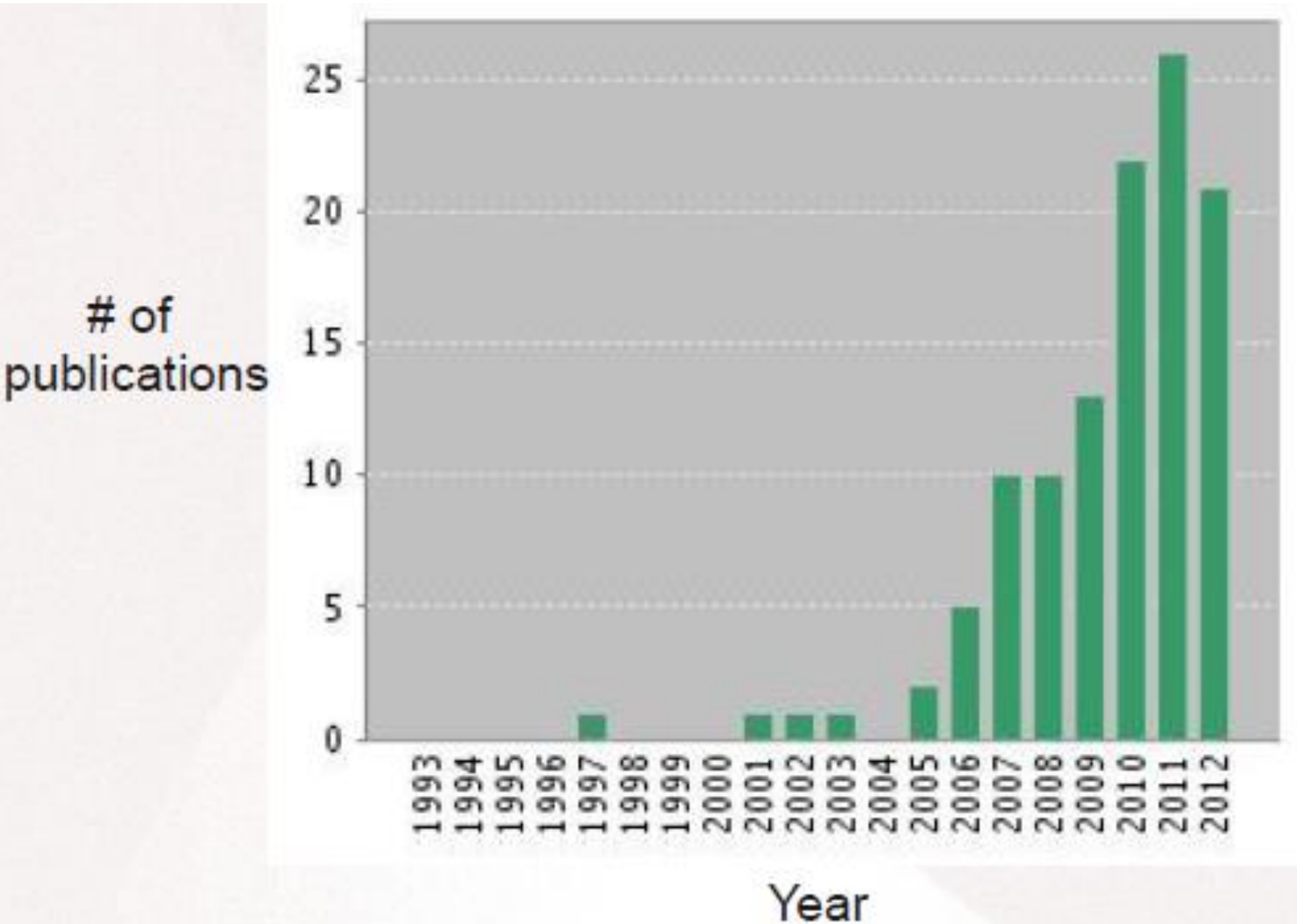
Metals are poor thermoelectric materials because of low Seebeck coefficient and large electronic contribution to thermal conductivity.

Here comes another talk on fundamental limits



A. Majumdar Science 303, 777(2004)

In five decades the *ZT* of semiconductors has increased only marginally, from about 0.6 to 1



# of publications
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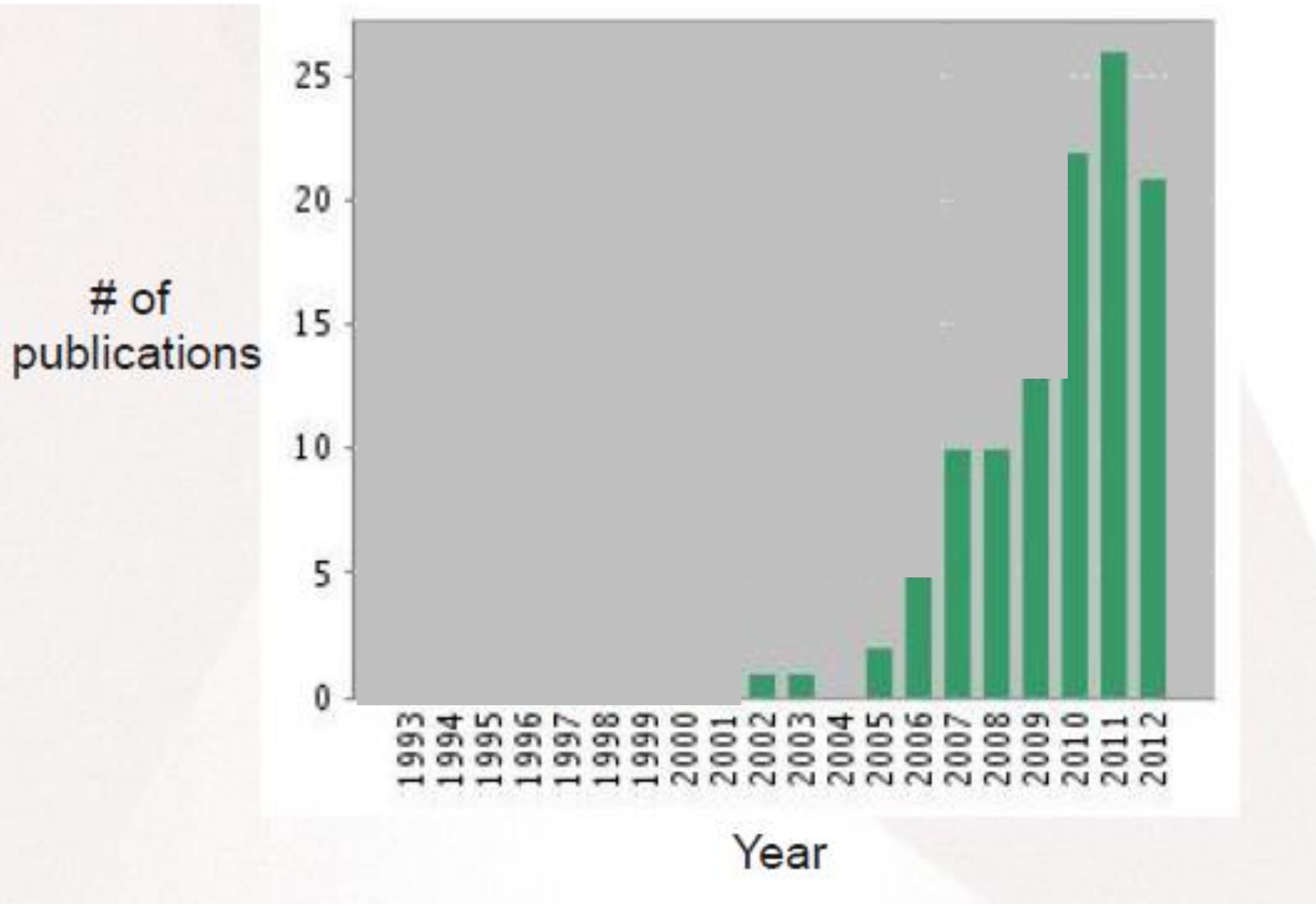

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1993
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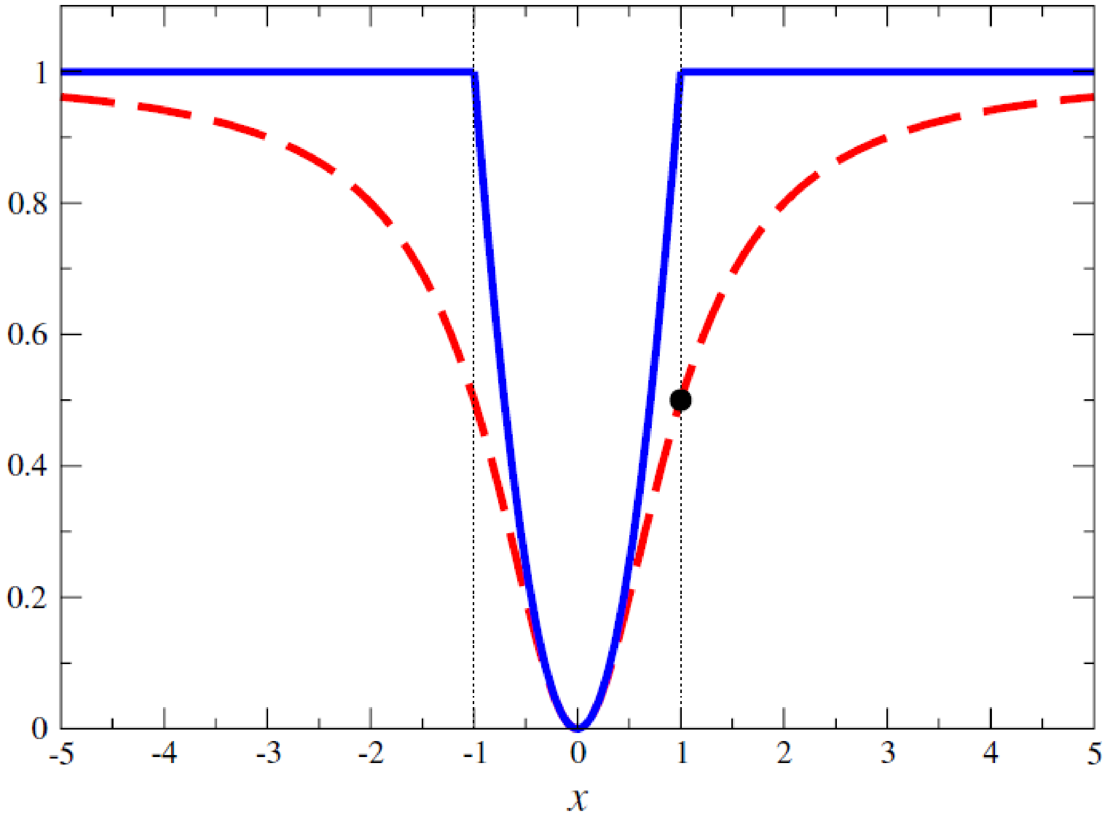
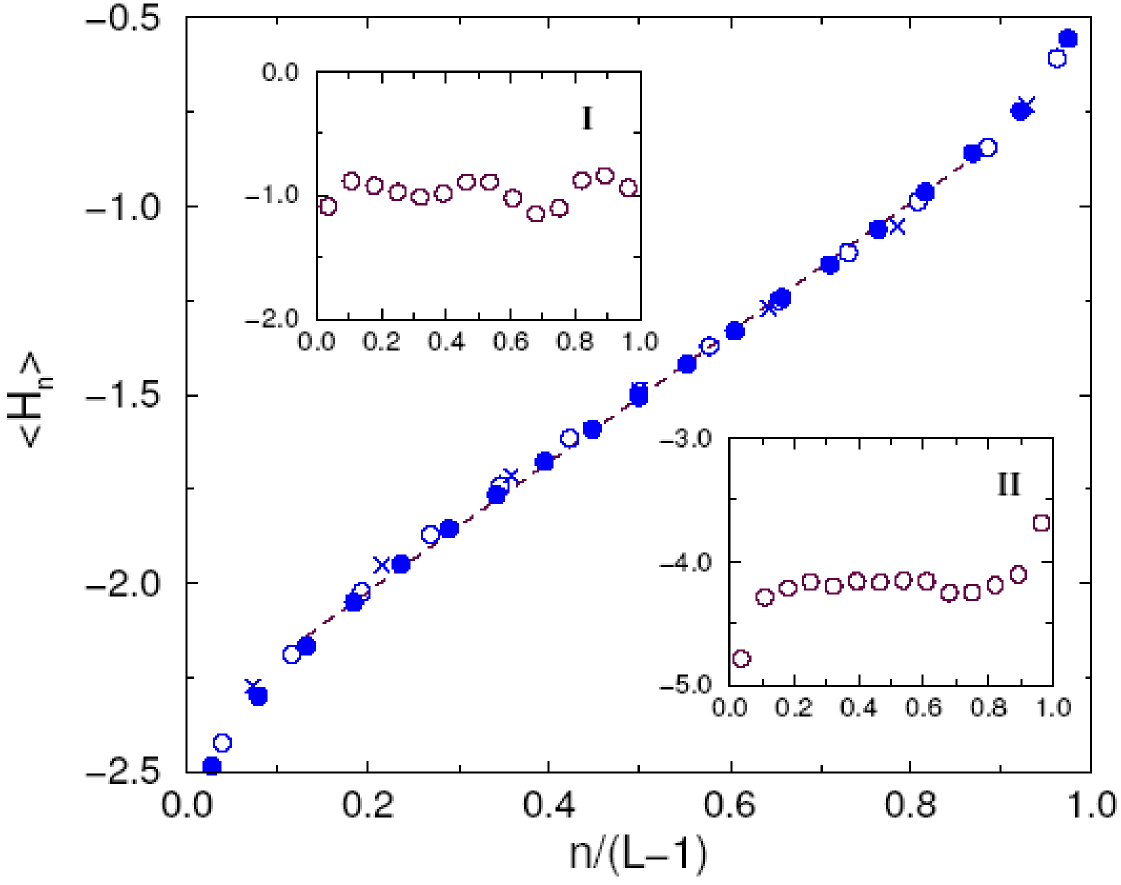
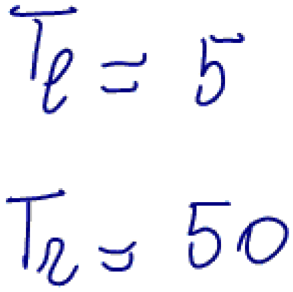
$$\eta_{\max} = \eta_C x \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1} \leq \eta_M = \begin{cases} \eta_C x^2 & \text{if } |x| \leq 1 \\ \eta_C & \text{if } |x| \geq 1 \end{cases}$$

$$\eta(\omega_{\max}) = \eta_{CA}^{(l)} \frac{xy}{2+y} \leq \eta^\star = \eta_C \frac{x^2}{x^2+1}$$



G. Benenti, K. Saito and G.C. prl 106 230602 (2011)





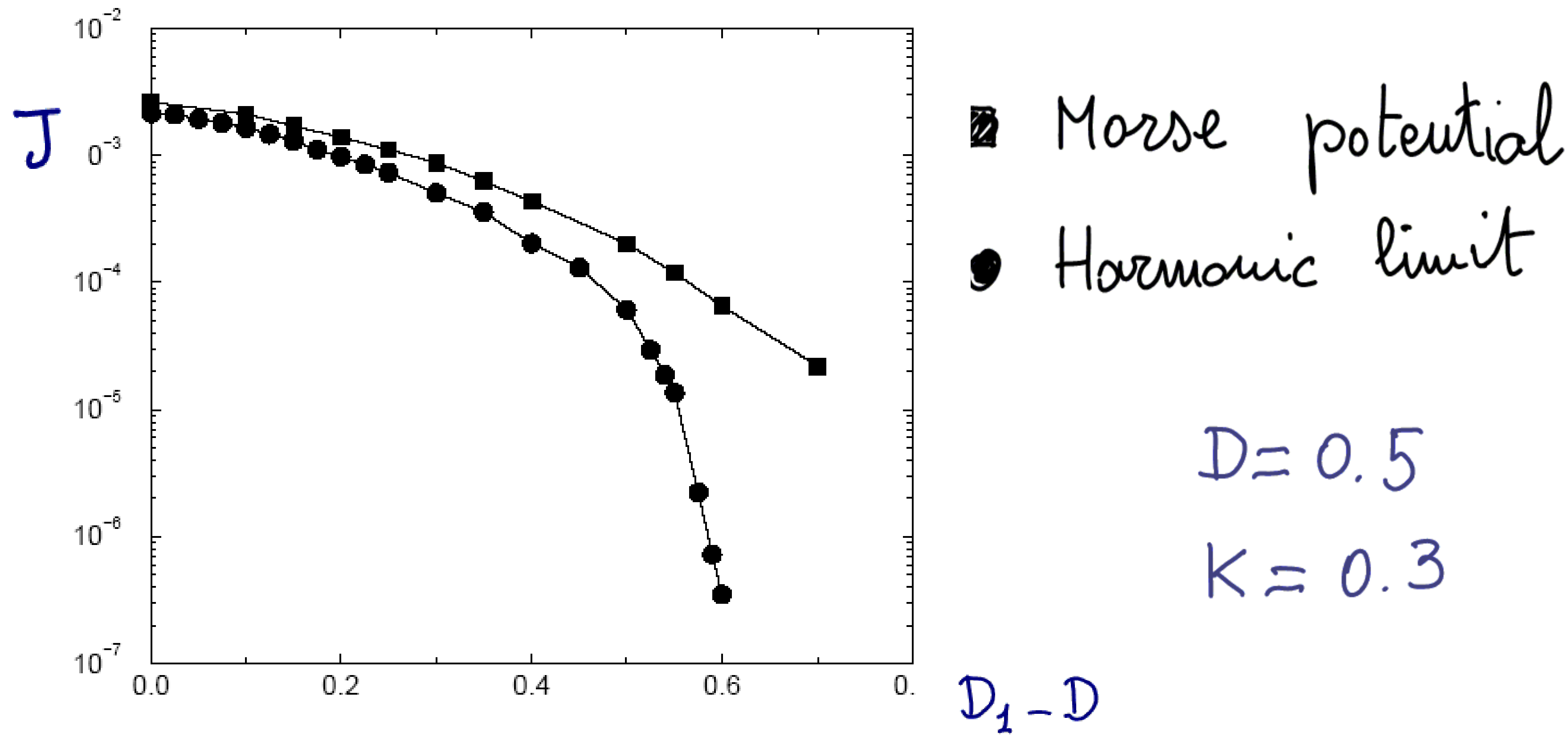
Energy profile for an out of equilibrium simulation

- **Linear in chaotic case**
- **Constant in integrable case**

We consider an Ising chain of L spins 1/2 with coupling constant Q subject to a uniform magnetic field $\vec{h} = (h_x, 0, h_z)$, with open boundaries. The Hamiltonian reads

$$\mathcal{H} = -Q \sum_{n=0}^{L-2} \sigma_n^z \sigma_{n+1}^z + \vec{h} \cdot \sum_{n=0}^{L-1} \vec{\sigma}_n \ , \qquad (1)$$

This interaction thus (periodically) resets the value of the local energy $h\sigma_{1,\mathrm{r}}$ of the spins in contact with the reservoirs. This information is then transmitted to the rest of the system during its dynamical evolution and relaxation towards equilibirum.


J
10-2
0-3
10-4
10-5
10-6
10-7
0.0
0.2
0.4
0.6
0.
Morse potential
Harmonic limit
D = 0.5
K = 0.3
D1 - D

$$H = \sum_{i=n,N} \frac{p_n^2}{2m} + \tilde{D}_n y_n^2 + \frac{1}{2} K (y_n - y_{n-1})^2$$

$$y_n(t) = e^{ikn - i\omega t}$$

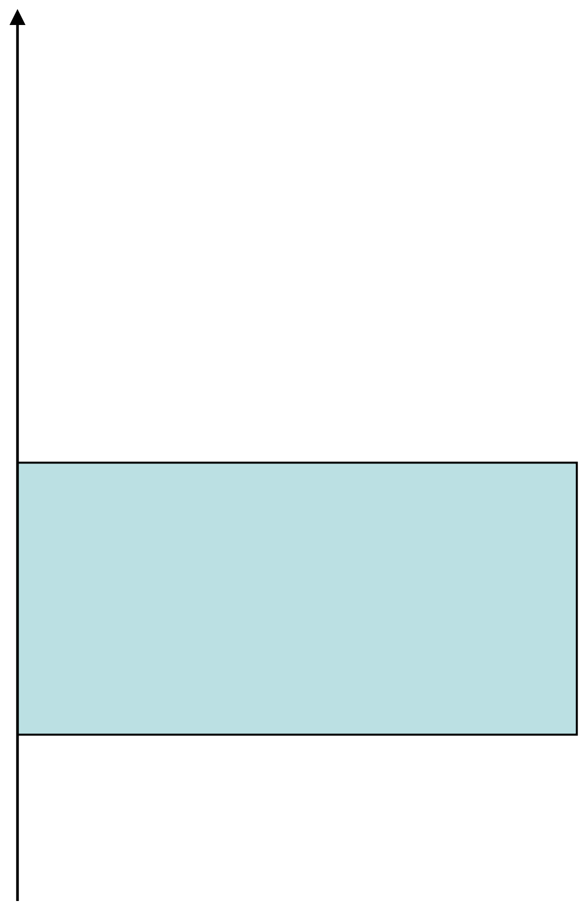
Plane waves solutions

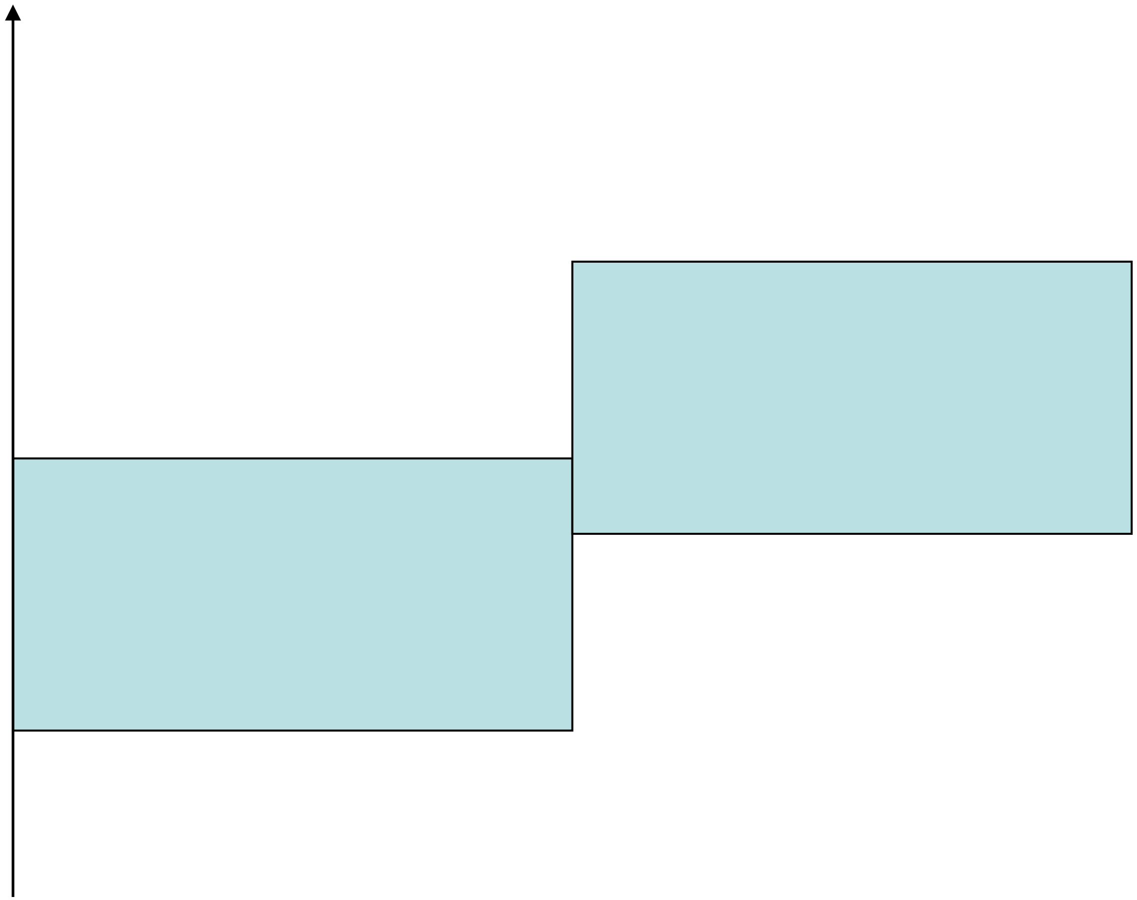
$$\omega^2 = 2K + 2\tilde{D} - 2K \cos k$$

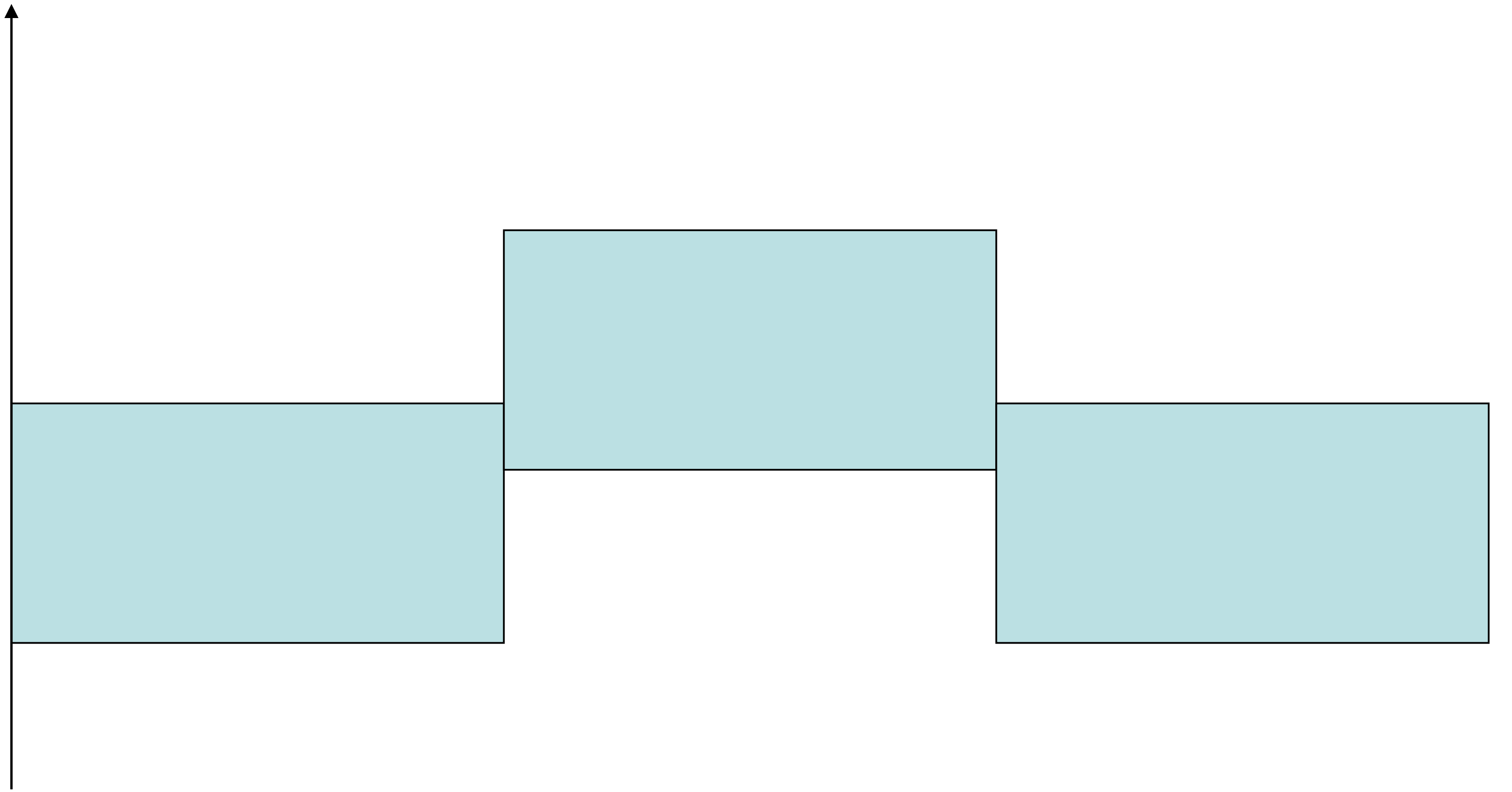
Dispersion relations

$$2\tilde{D} \le \omega^2 \le 2\tilde{D} + 4K$$

Phonon band

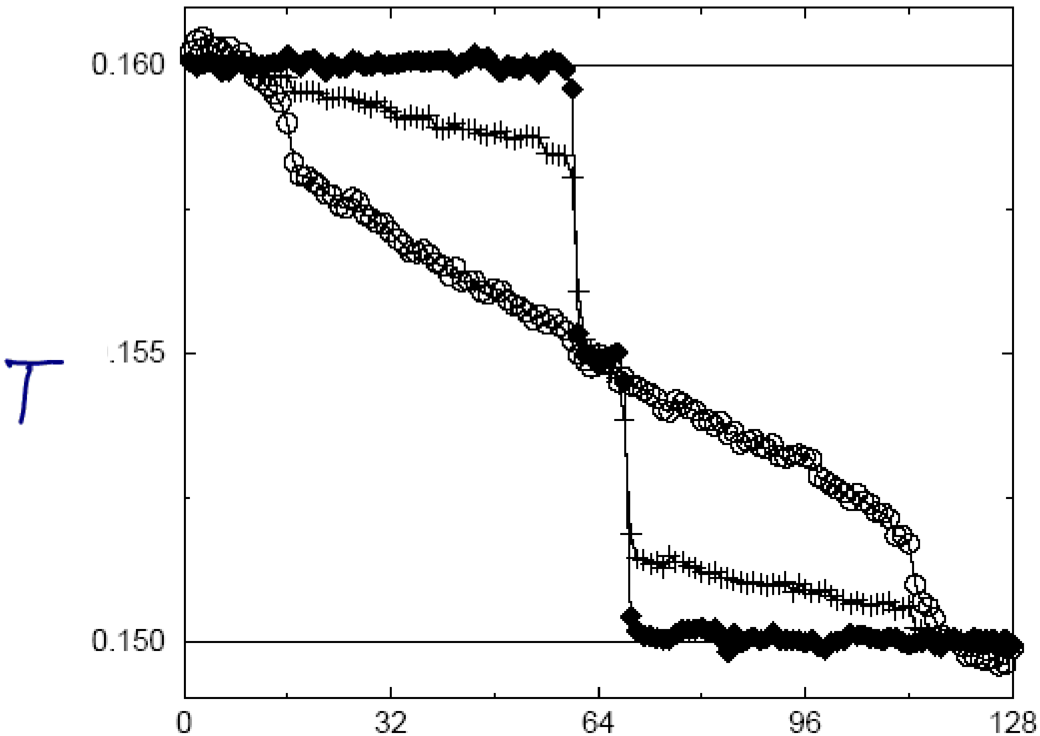






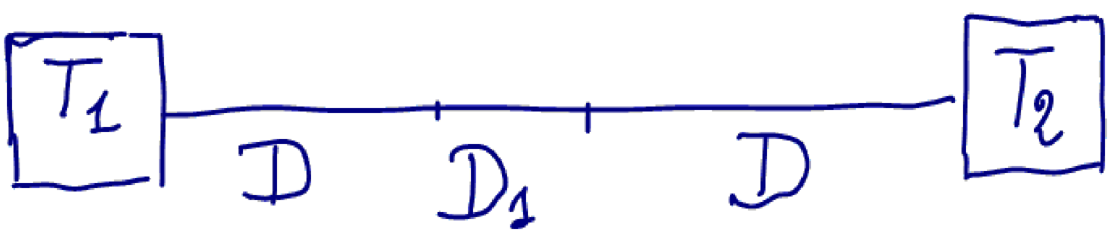
INTERNAL TEMPERATURE PROFILE

$D = 0.5$



$(K = 0.3)$

$(\alpha_n = \alpha = 1)$



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:

$$J_u \propto J_\rho$$

If there is a single, relevant, constant of motion, M=1 due to Suzuki formula:

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

The ballistic contribution to det L vanishes thus implying that det L increases slower than Λ^2

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

Then $\kappa \propto \det L / L_{\rho\rho}$

$$\kappa \propto \Lambda^{\alpha}, \text{ with } \alpha < 1$$

sub-ballistic

If M>1 then $\det L \propto \Lambda^2$ ballistic transport

therefore $ZT \propto \Lambda^0$

Indeed due to Schwartz inequality:

If M>1 then $\det L \propto \Lambda^2$ **ballistic transport**

therefore $ZT \propto \Lambda^0$

Indeed due to Schwartz inequality:

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

where

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

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

Analytical results for 1d gas

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

$$D_{\rho\rho}(\Lambda) = \frac{C_{\rho\rho}(\Lambda)}{2\Lambda} = \frac{TN^2}{2\Lambda(\nu_1 N_1 + \nu_2 N_2)}$$

$$N = N_1 + N_2$$

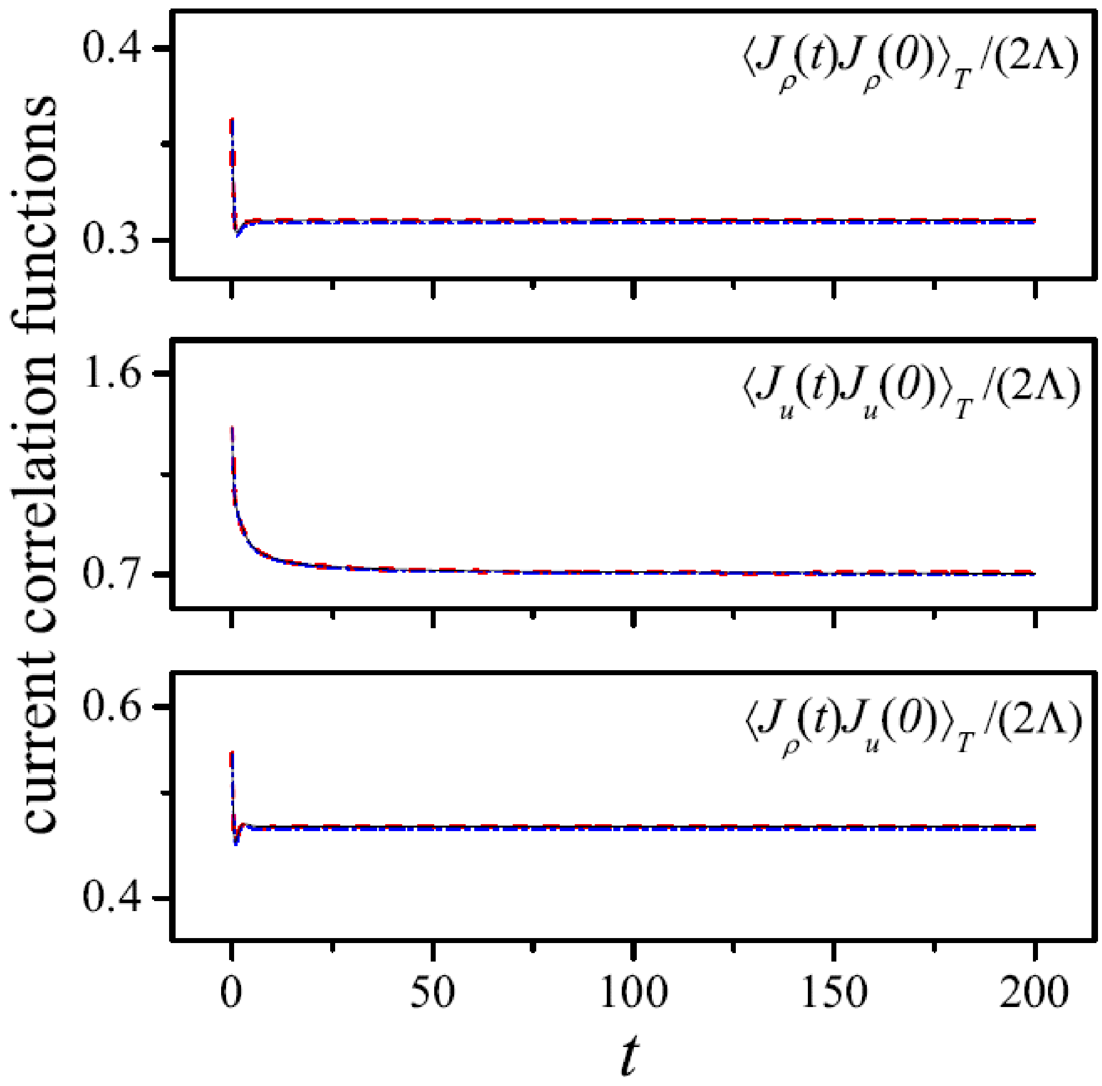
$$D_{uu}(\Lambda) = \frac{C_{uu}(\Lambda)}{2\Lambda} = \frac{9T^3N^2}{8\Lambda(\nu_1 N_1 + \nu_2 N_2)}$$

$$D_{\rho u}(\Lambda) = \frac{C_{\rho u}(\Lambda)}{2\Lambda} = \frac{3T^2N^2}{4\Lambda(\nu_1 N_1 + \nu_2 N_2)}$$

$$D_{\rho\rho}(\Lambda) D_{uu}(\Lambda) - D^2_{\rho u}(\Lambda) = 0$$

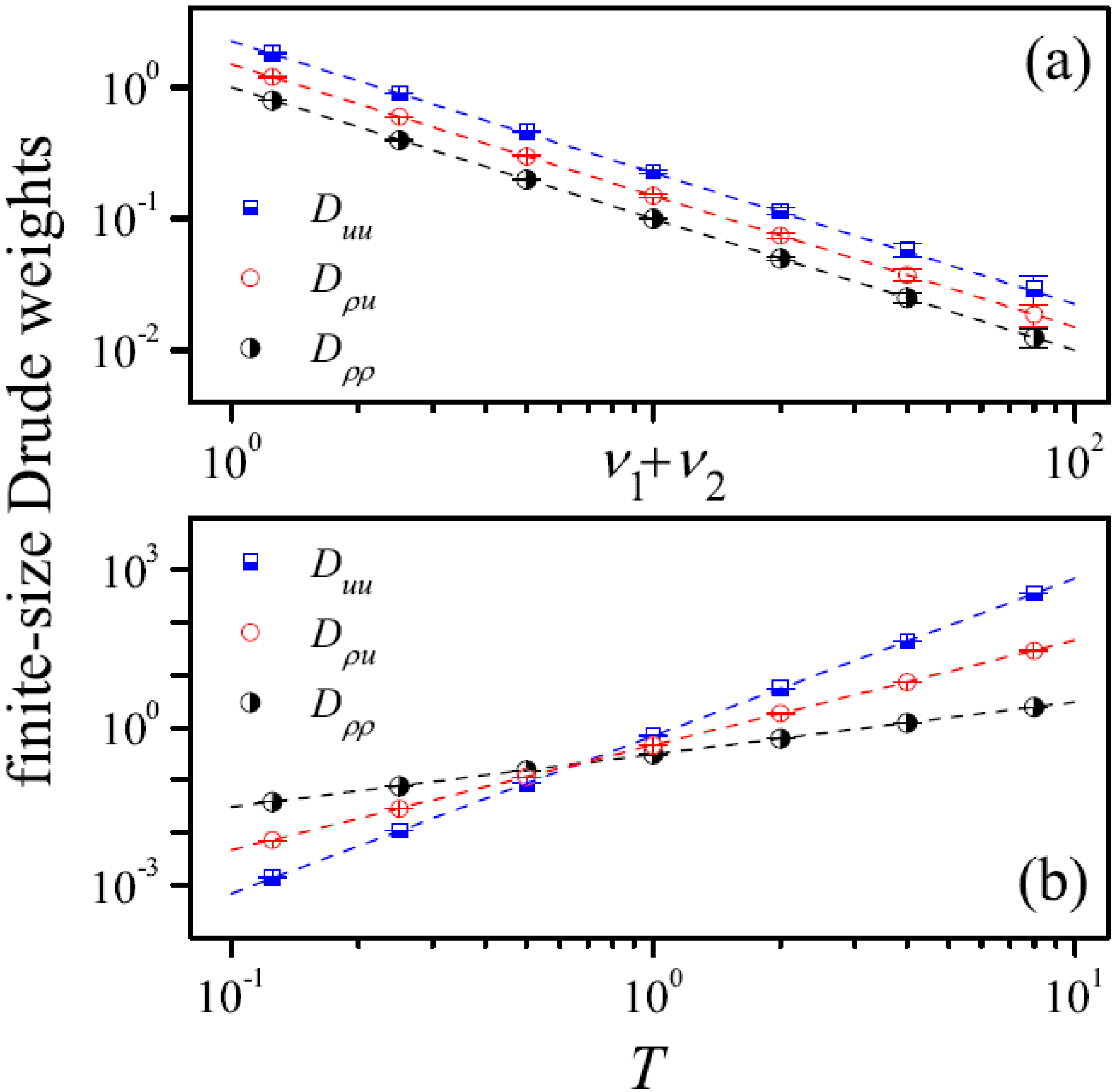
$$S = L_{\rho u}/T L_{\rho\rho} \quad = 1.5$$

Numerical results: correlation functions (p.b.c.)



$$C_{ij}(\Lambda) = \lim_{t\to\infty} c_{ij}(\Lambda, t)$$

From time-averaged correlation functions we can estimate the finite-size Drude weights



Lettere al Nuovo Cimento **28 (1980) 279**

On the Connection between Quantization of Nonintegrable Systems and Statistical Theory of Spectra (*).

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I. GUARNIERI

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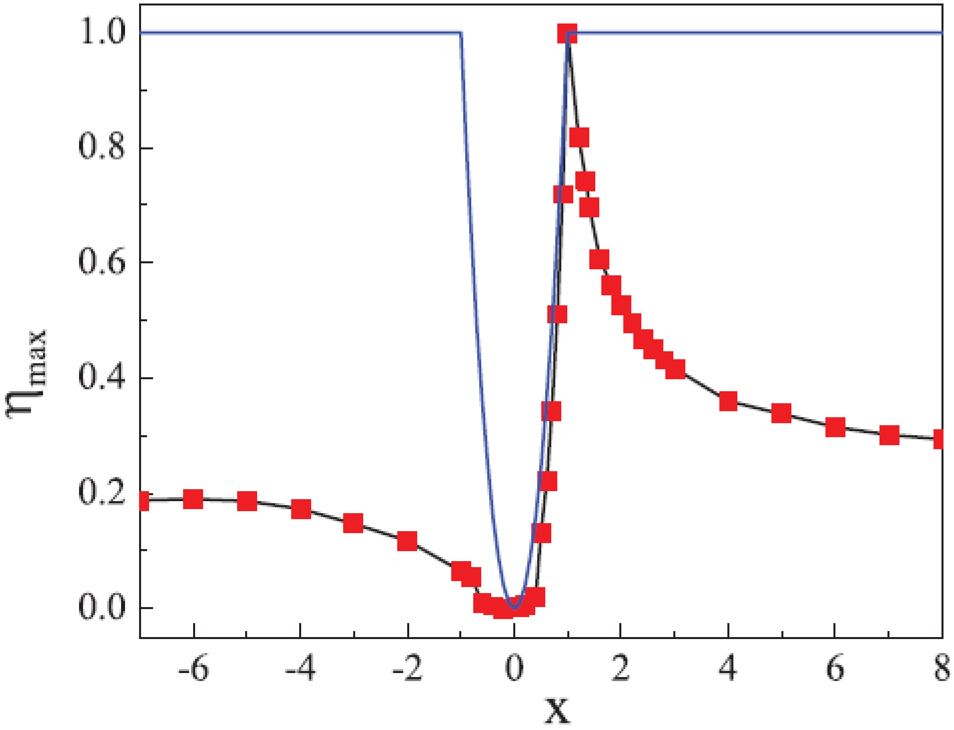
The present letter is motivated by a certain obscurity inherent in the comparison of seemingly disparate objects, such as an ensemble of matrices (a « random matrix ») and a single, classically stochastic Hamiltonian. For example, it is not clear how to relate the $P(s)$ obtained by averaging over a Gaussian ensemble and the $P(s)$ obtained by computing frequencies in the spectral sequence of one classically « stochastic » Hamiltonian. (More precisely, $P(s)$ should be the limit of frequencies in the finite

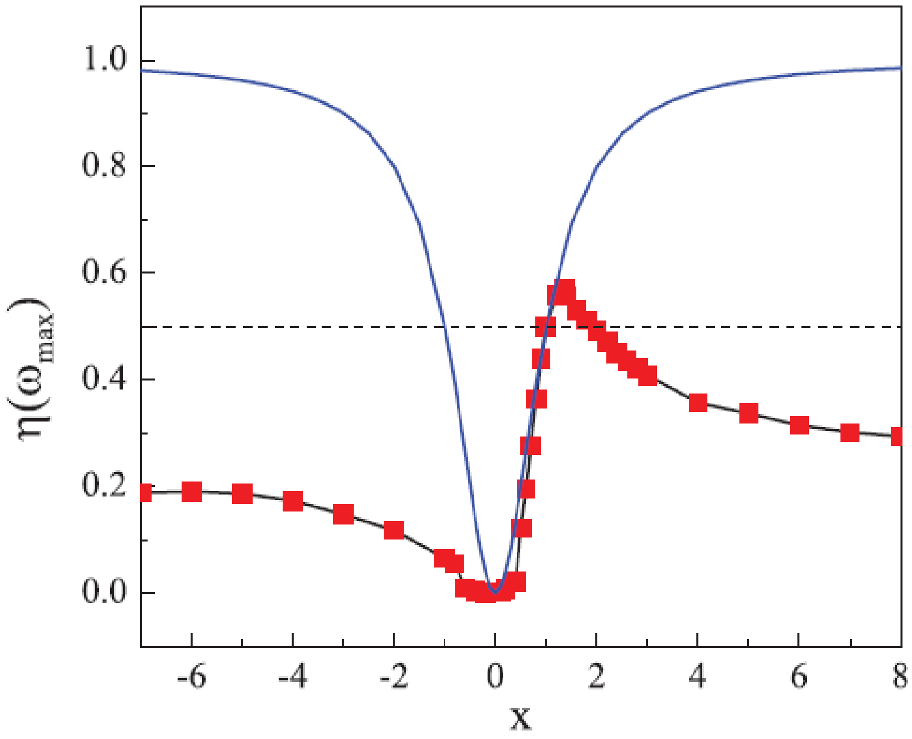
devices used for cooling, and for power generation

Voyager mission to Jupiter and Saturn, here at its launch in 1977.



Maximum efficiency

V. Balachandran, G. Benenti, G.C., PRB 87, 165419 (2013)



Efficiency at maximum power

Curzon-Ahlborn limit

V. Balachandran, G. Benenti, G.C., PRB 87, 165419 (2013)

Efficiency at maximum power

$$\eta_{CA} = 1 - \sqrt{T_2/T_1}$$

Curzon -Ahlborn
upper bound

In this talk:

- Fourier law in classical and quantum mechanics

- can we control the heat current? - Thermal rectifiers

- Thermoelectric efficiency

- beyond thermodynamic restrictions