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).

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

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

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

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

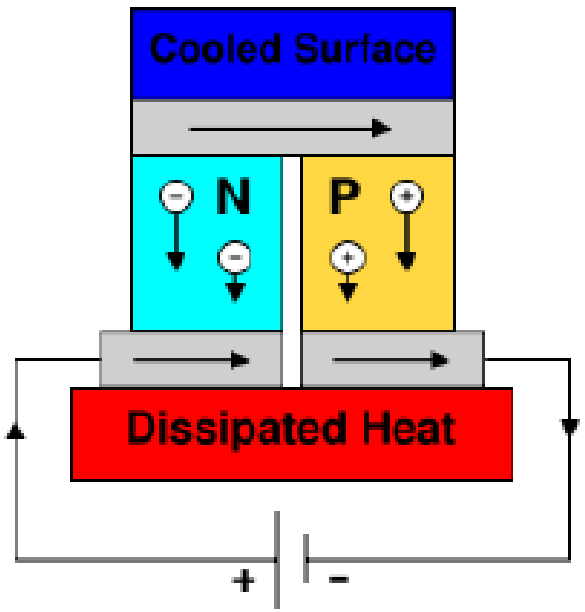
Curzon -Ahlborn upper bound

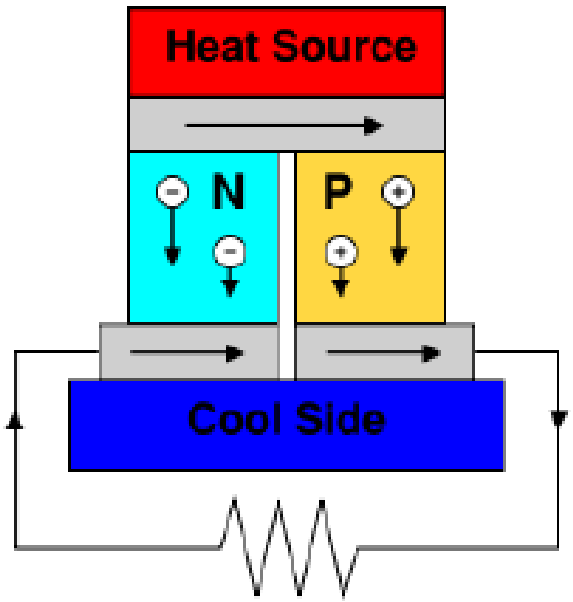
POWERFUL HEAT

How to increase efficiency of thermopower generation and refrigeration?

A dynamical systems approach

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

The ZT figure of merit

$\sigma \equiv$ electrical conductivity

$S \equiv$ Seebeck coefficient

$k \equiv$ thermal conductivity

$T \equiv$ absolute temperature

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

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

In linear response regime:

$$\eta_{max} = \eta_c \frac{\sqrt{ZT+1} - 1}{\sqrt{ZT+1} + 1}$$ maximum efficiency

$$\eta(\omega_{max}) = \frac{\eta_c}{2} \frac{ZT}{ZT+2}$$ efficiency at maximum power

In both cases maximum is reached for

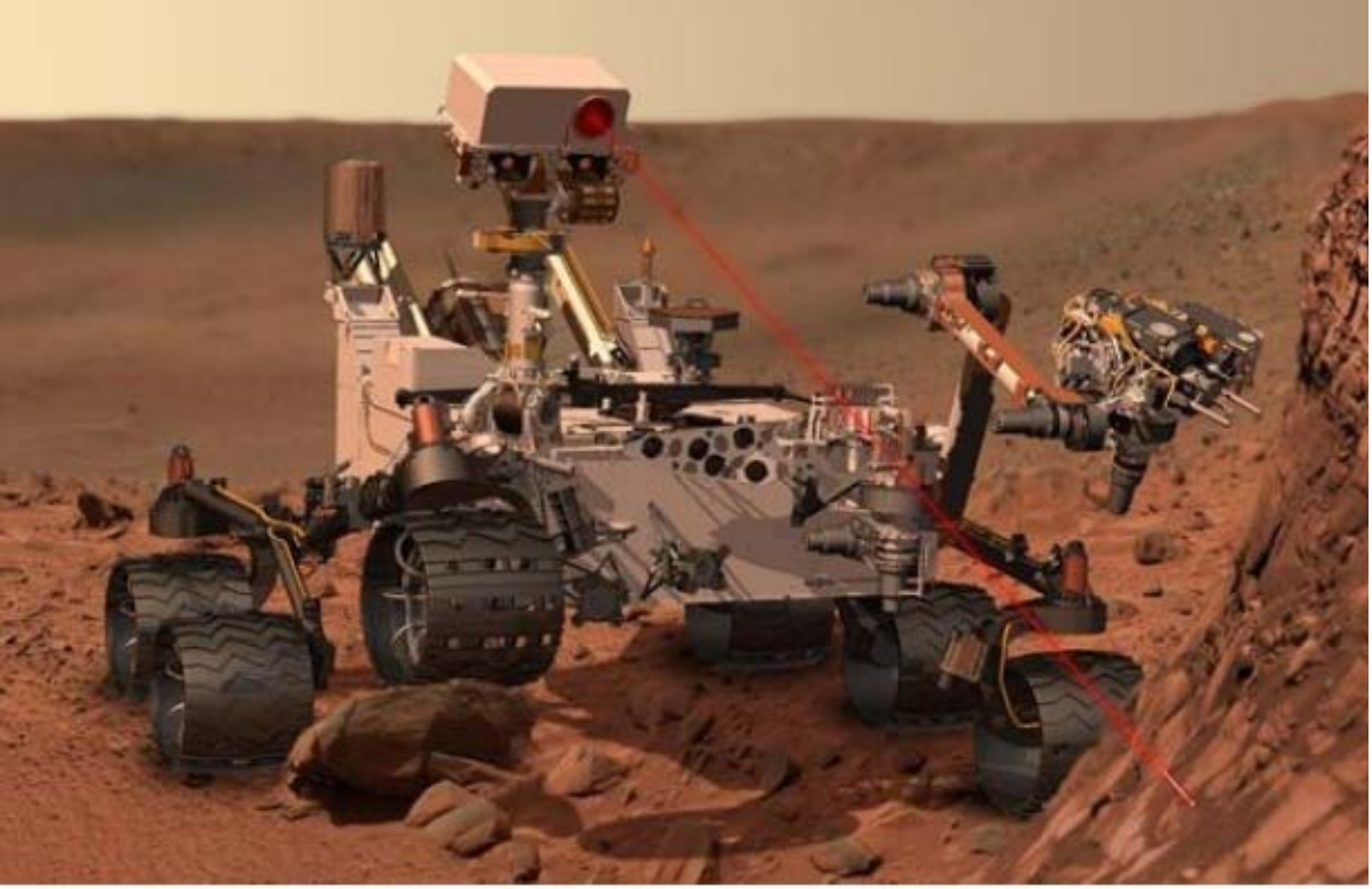
$$ZT \to \infty$$

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.



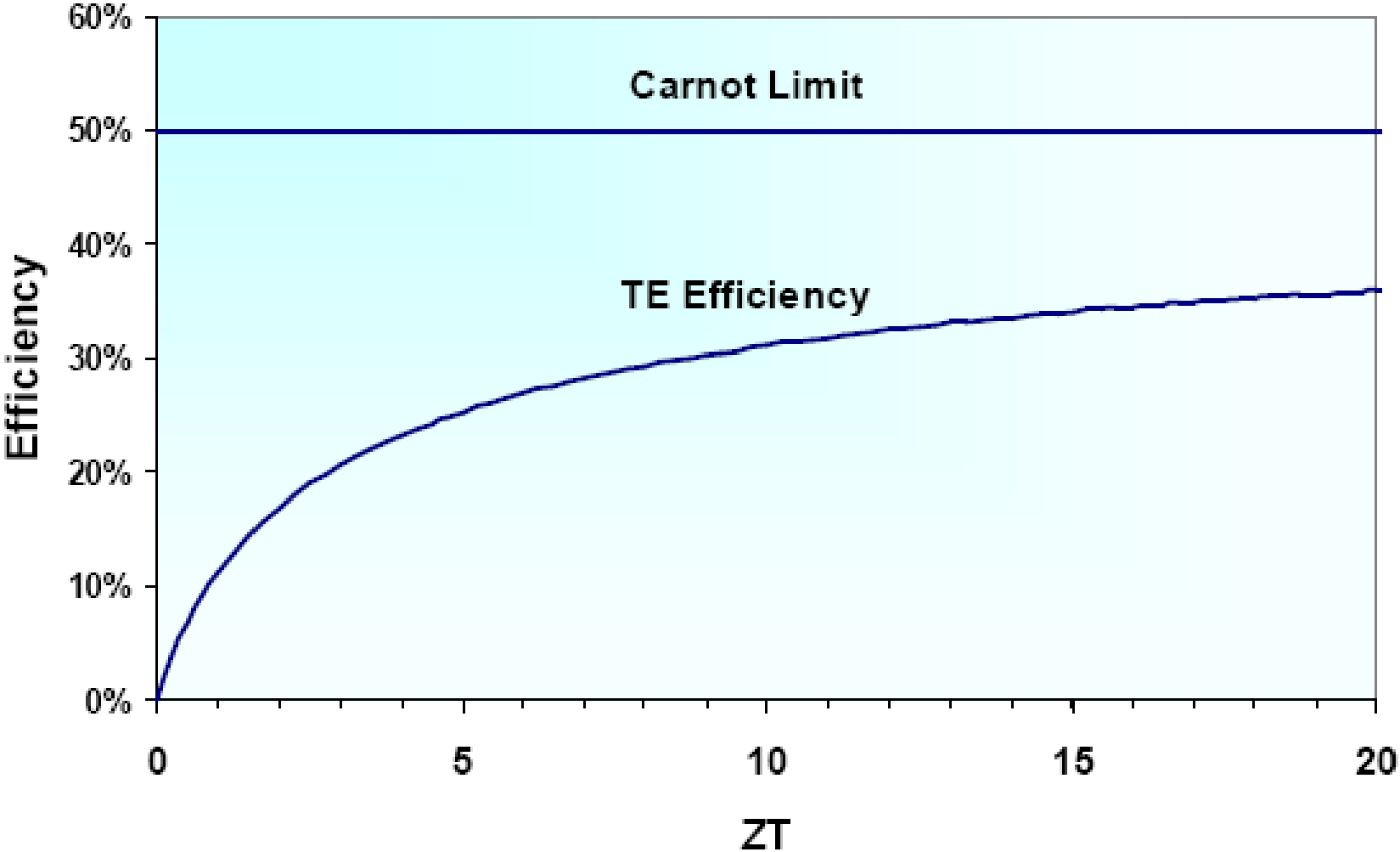
MARS SCIENCE LABORATORY -Robotic space probe- **august 2012**

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


BioLite

New funding. In the early 1990s **DARPA** and the **Office of Naval Research** initiated support for basic thermoelectric materials research: thermoelectric coolers are used for **night vision, sensors, guidance systems, etc**. and even modest efficiency gains might make TE air conditioning practical in **submarines** (TE cooling is quiet) and enhance the existing DoD applications.

USS DOLPHIN AGSS 555 – Test for Silent Running



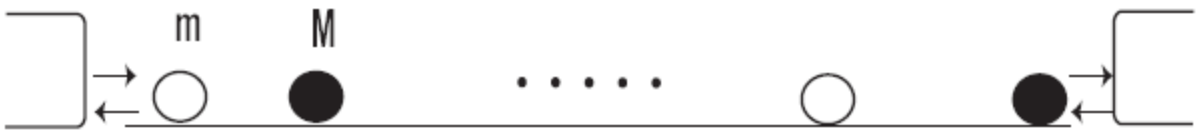
Best thermoelectric material have ZT around 1

ZT> 3 is required in order to be competitive with mech power generators and refrigerators

Interacting system

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

$m \neq M$



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

For $m \neq M$ $\quad ZT = N^{\alpha} \quad \alpha \sim 0.7$

G. Benenti, G.C., Wang Jiao: phys.rev.lett. (2013)

The quantum suppression of deterministic classical diffusive behaviour takes place after a

relaxation time scale $\boxed{t_R \sim 1/\hbar^2}$

Inside this time, quantum motion mimics the classical diffusive behaviour even though the quantum "chaotic" motion is dynamically stable since it is exponentially unstable only inside the

random time scale $\boxed{t_r \sim \ln\hbar}$

Exponential instability is sufficient for a meaningful statistical description.

-Is it also necessary?

-Exponential decay of correlations?

The triangle map: A model of Quantum chaos

Casati, Prosen phys. rev. Lett. 2000

$$y_{n+1} = y_n + \alpha \, \mathrm{sgn} x_n + \beta \qquad (\mathrm{mod} 2),$$

$$x_{n+1} = x_n + y_{n+1} \qquad (\mathrm{mod} 2),$$

$$\det J = 1, \mathrm{tr} J = 2$$

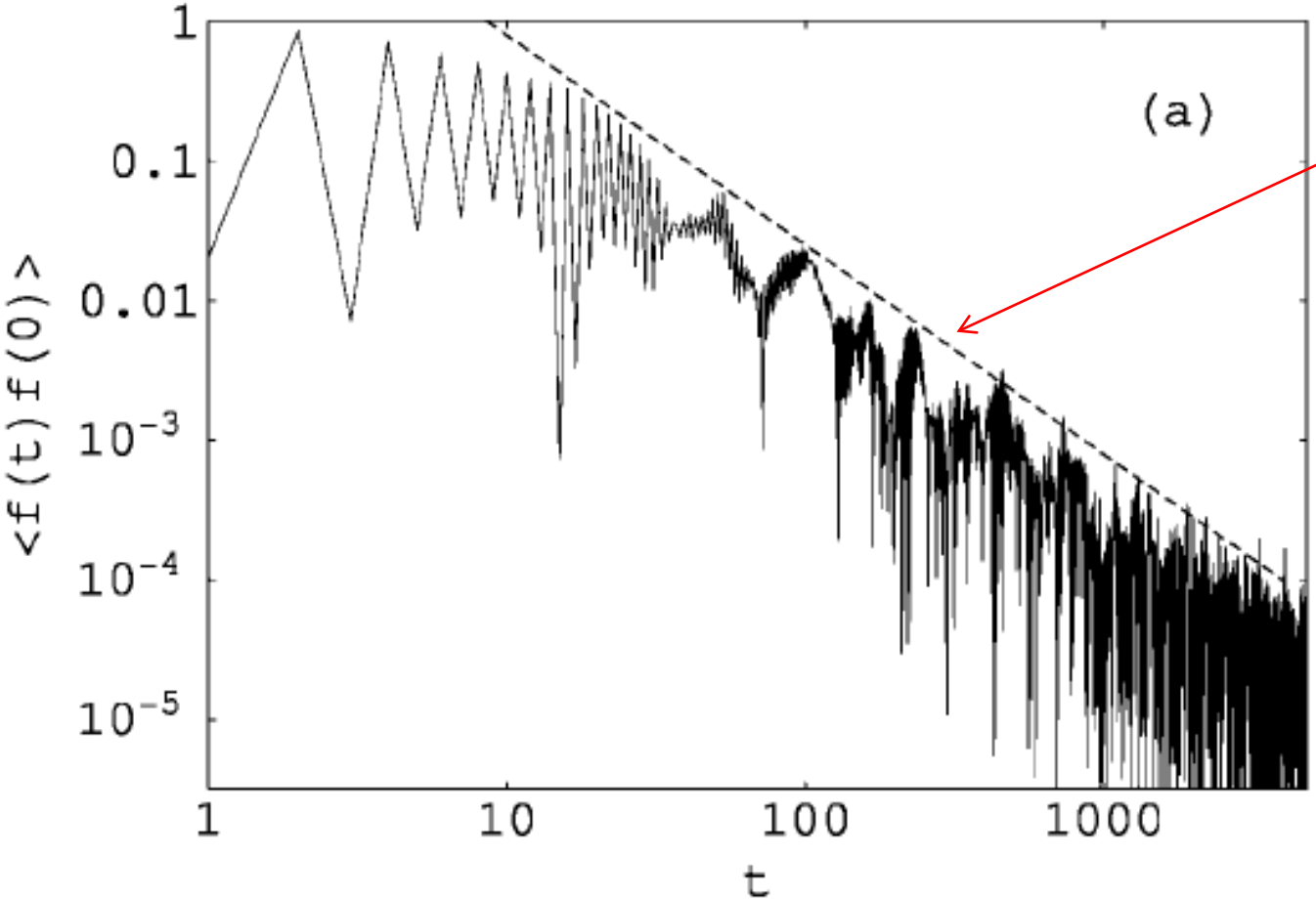
(parabolic map)

$$\alpha = (\tfrac{1}{2}(\sqrt{5} - 1) - e^{-1})/2$$

$$\beta = (\tfrac{1}{2}(\sqrt{5} - 1) + e^{-1})/2$$

Correlations decay

$$f = \cos(\pi y)$$



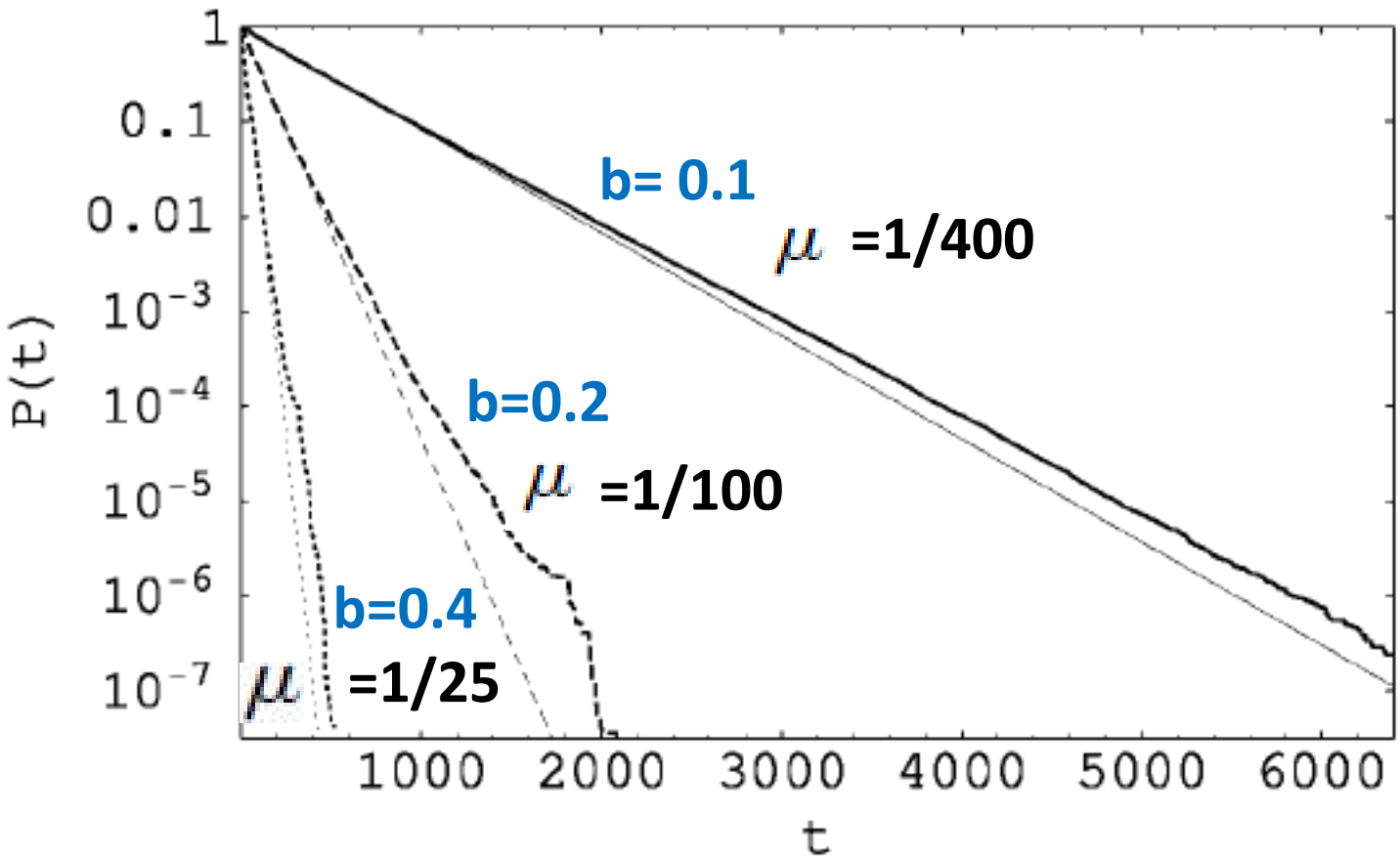
slope= -3/2

Exponential decay of Poincare recurrences

Probability P(t) for an orbit to stay outside the set $\mathcal{A} = [0, b] \times [0, b]$

for a time longer than t.

$$P_i(t) = \exp(-\mu t) \qquad \mu = |\mathcal{A}|$$



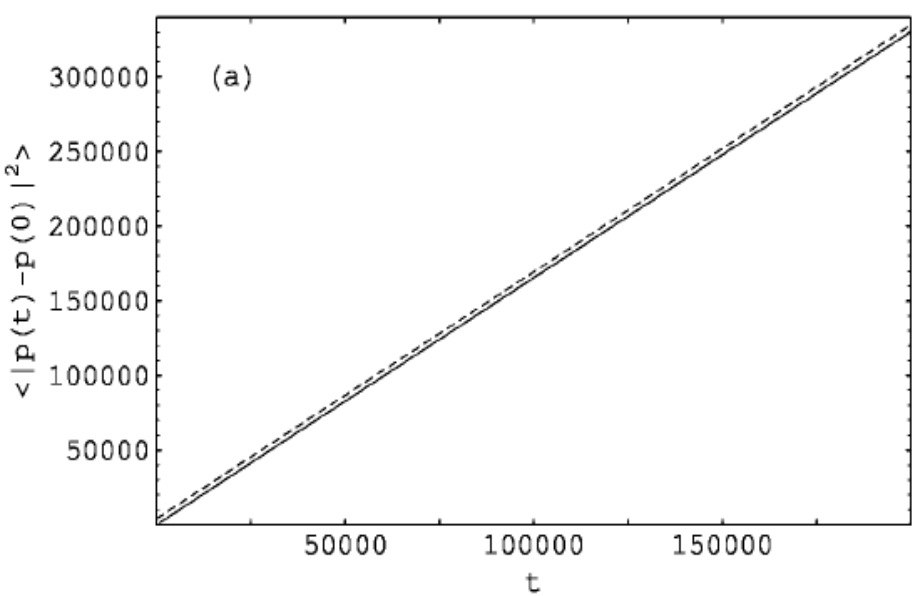
Diffusion

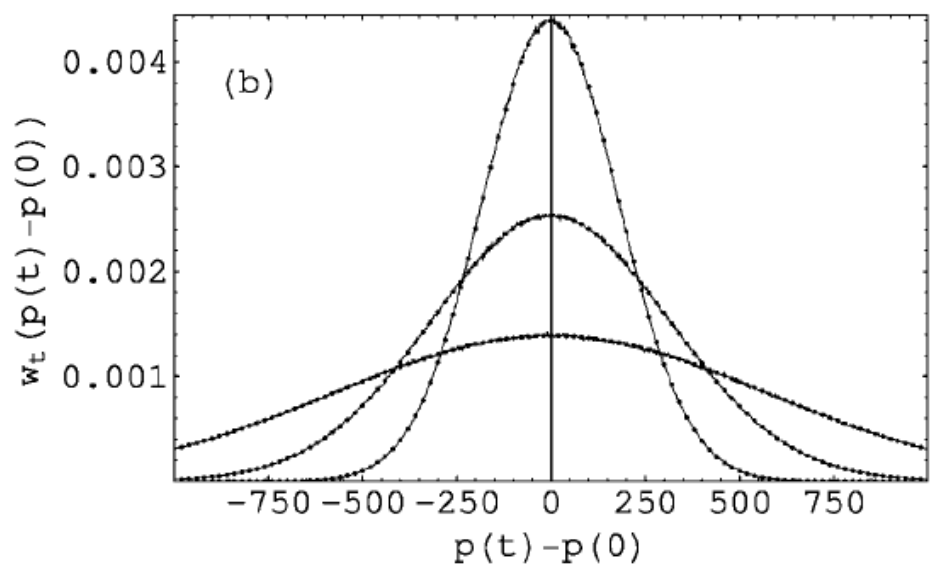
Consider the map on the cylinder (in integer variable “p”)

$$y_n = y_0 + \beta n + \alpha p_n$$

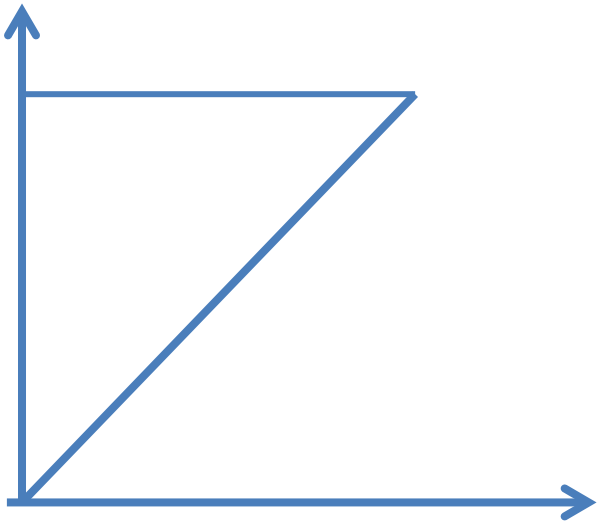
$$\langle (p_{n+t} - p_n)^2 \rangle = \langle p_t^2 \rangle = Dt$$

The dotted curves are solutions of diffusion eq. with variance Dt





rescaling



The speed is conserved by collisions:

In the velocity space the overall dynamics can be described as a rotation by an angle

Starting with initial value the final value after a finite sequence can be written as

In terms of the integer K the dynamics reduces to the map

$$K' = -K+1$$ Particles collision

$$K' = -K$$ Boundary collision

JOURNAL OF COMPUTATIONAL PHYSICS 20, 97–109 (1976)

Computer Study of Ergodicity and Mixing in a Two-Particle, Hard Point Gas System

GIULIO CASATI AND JOSEPH FORD

Received June 9, 1975

Computer experiments performed on the unequal-mass, two-particle hard point gas are discussed and shown to provide evidence for ergodic and mixing behavior…

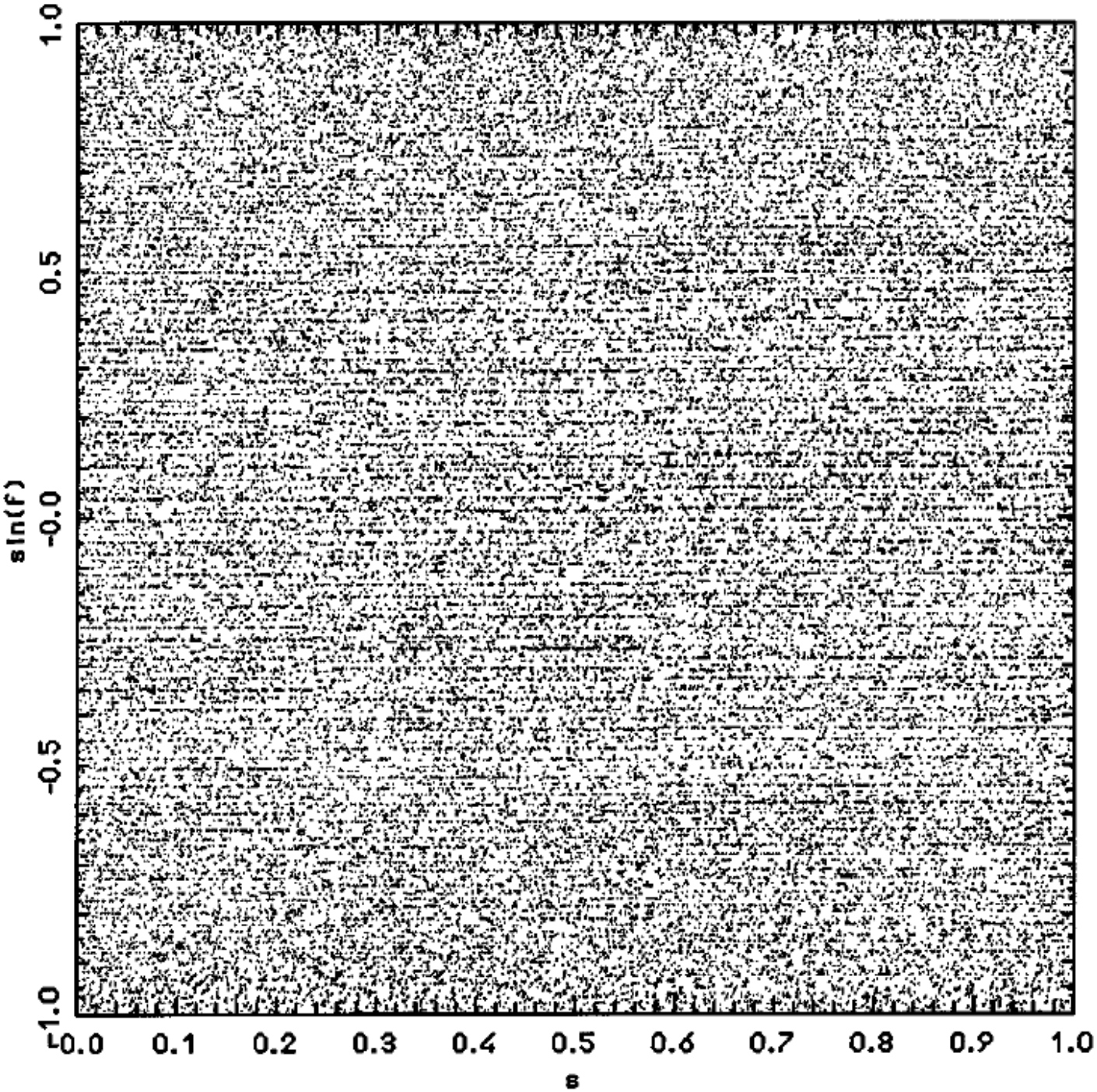
"The only surprise in these calculations, was the rather large total number of collisions required to observe all 4n velocity-pairs. Indeed, initially we believed that some unsuspected constant of the motion…."

PHYSICAL REVIEW E VOLUME 55, NUMBER 6 JUNE 1997

Numerical study on ergodic properties of triangular billiards

Roberto Artuso,[1,2] Giulio Casati,[1,2] and Italo Guarneri[1,3]

"We consider the motion of a point particle in right triangular billiards. By considering the global dynamics (when acute angles are not rationally connected to)we find numerical evidence for the <u>conjecture that the motion is ergodic and weakly mixing. "</u>


1.0
0.5
-0.0
-0.5
-1.0
s ln(f)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
s

MBER 23 PHYSICAL REVIEW LETTERS 6 DECEMBER 1999

Mixing Property of Triangular Billiards

Giulio Casati[1] and Tomaž Prosen[2]

We present numerical evidence which strongly suggests that irrational triangular billiards (<u>all angles irrational with</u>) are mixing.

"All the above lead to the conclusion that, <u>outside any reasonable doubt</u>, generic irrational triangles are mixing.

The particular case of right triangles is much less clear. The behavior of correlations in such a case is noisy and the exponent of the decay is too small to allow for any definite conclusion."

S. Kerckhoff, H. Masur, and J. Smillie, Ann. Math. 124, 293 (1986).

In the rational case $\alpha = 2\pi p/q$

an orbit with initial lie on a surface

Theorem:

Ergodicity of billiards in polygons: explicit examples

Ya. B. Vorobets

1996 Russ. Math. Surv. 51 756

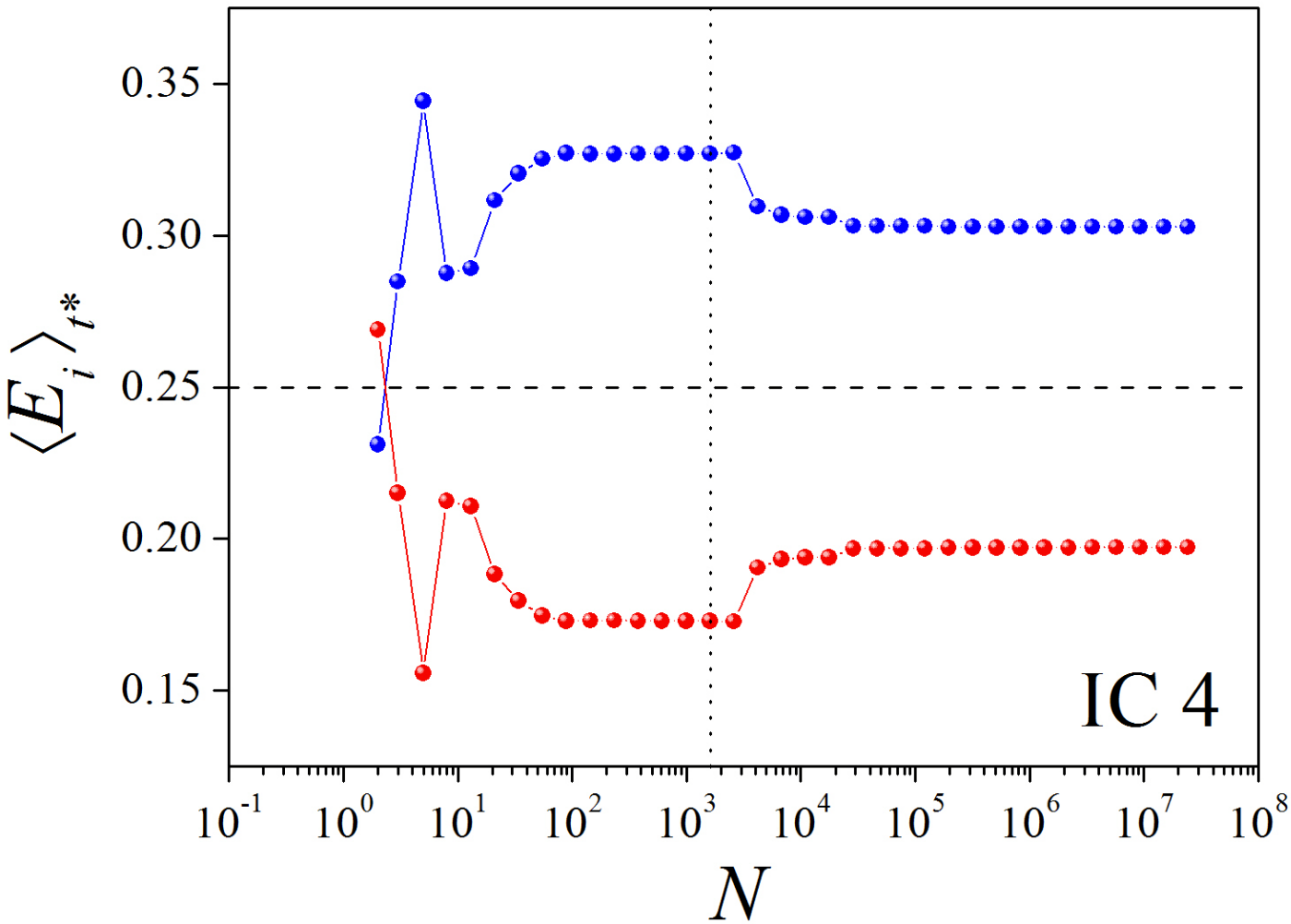
Theorem 1. *If the polygon Q admits approximation by rational polygons at the rate*

$$\delta(N) = \left({}_{2}2^{2^{2^{N}}} \right)^{-1},$$

$\pi n/N$

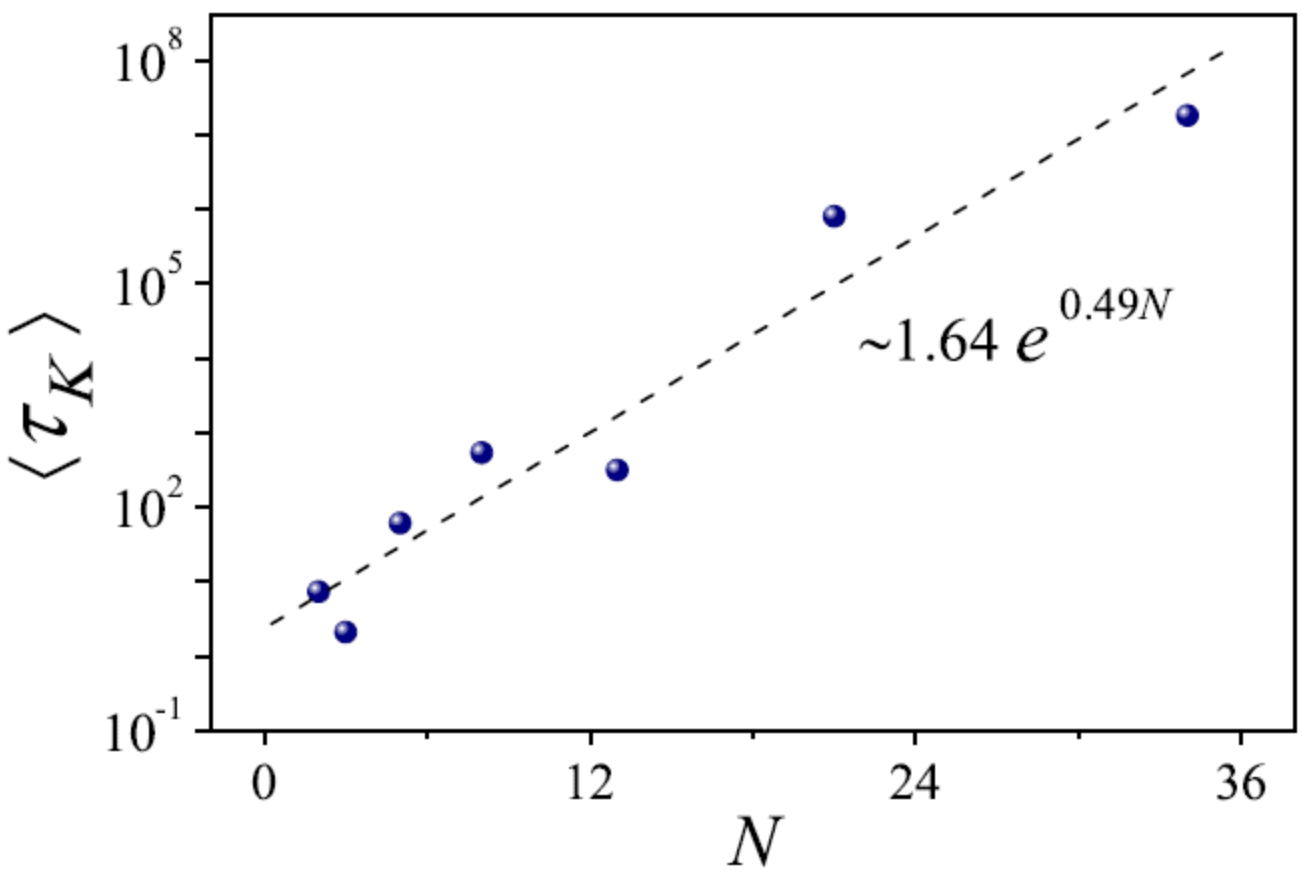
then the billiard flow in Q is ergodic.

For example, the billiard flow in a right-angled triangle with an acute angle equal to $\pi\left(a_5^{-1} + a_{10}^{-1} + \cdots + a_{5n}^{-1} + \cdots\right)$ is ergodic. Here $\{a_n\}$ is the sequence given by the relations $a_0 = 1$, $a_{n+1} = 2^{a_n}$ for $n = 0, 1, 2, \ldots$.


0.35
0.30
0.25
0.20
0.15
$\langle E_i \rangle_{t^*}$
IC 4
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
10^{8}
N

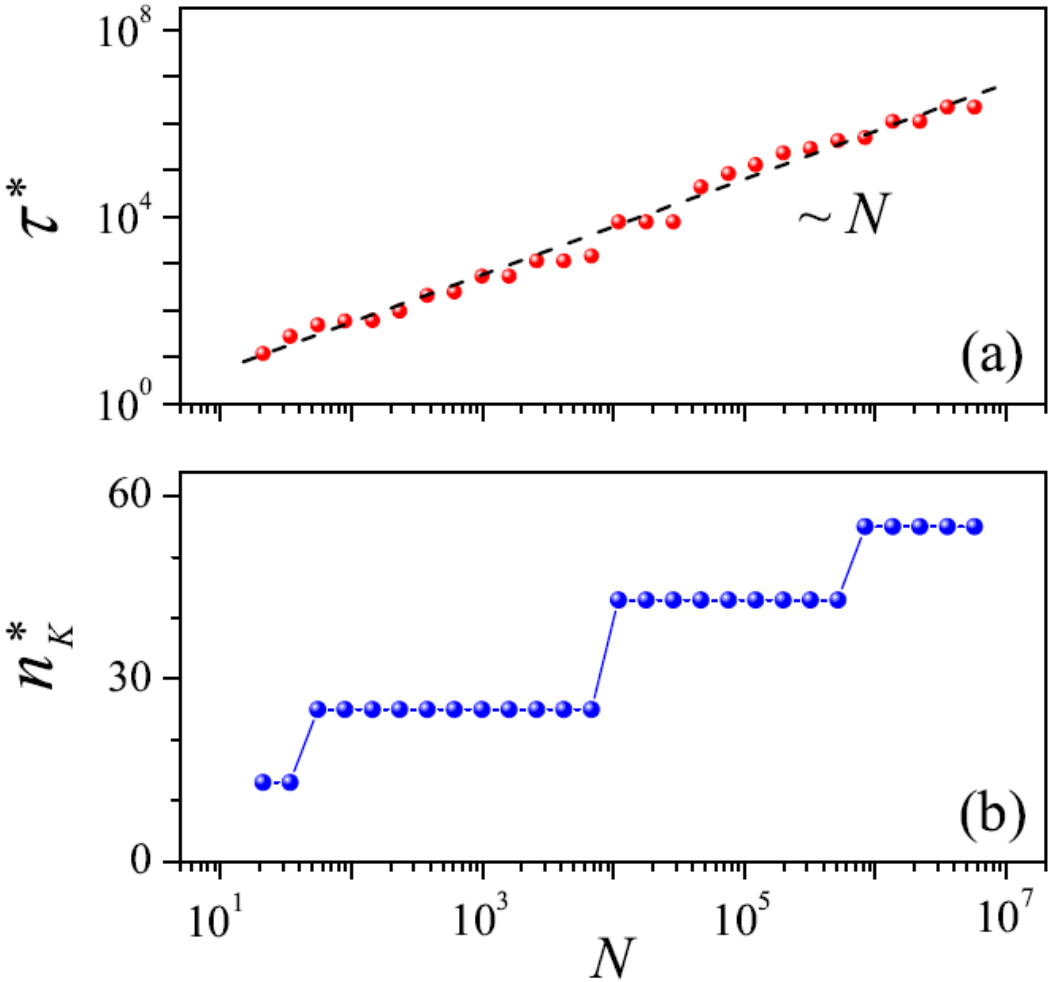
$$\alpha/\pi = (\sqrt{5}-1)/2$$ = M/N = 1/2, 2/3, 3/5, 5/8, 8/13, ...

The time required to the system to visit all the N allowed values of *K* increases exponentially with N.

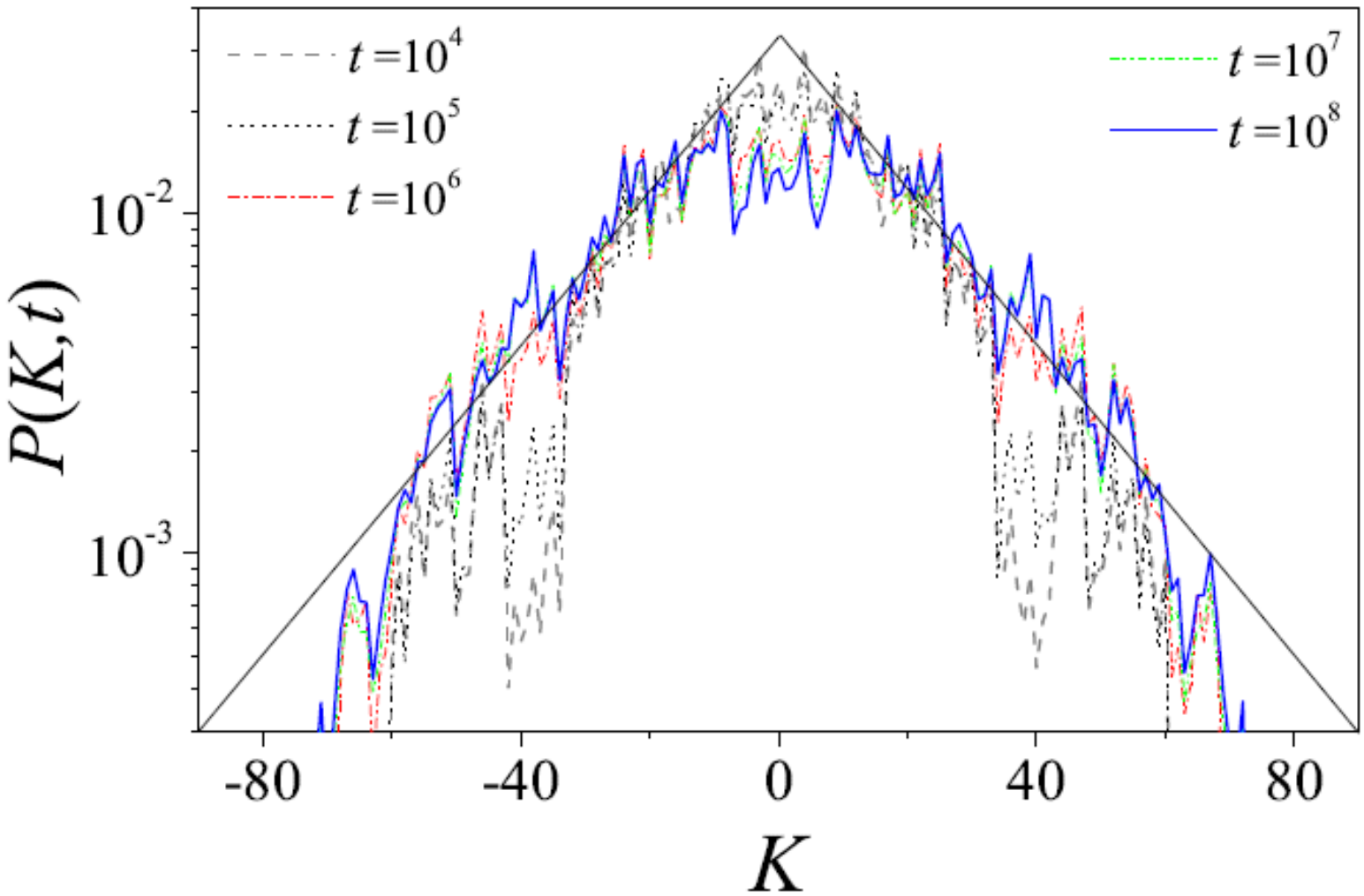


$\alpha/\pi = M/N$ = 1/2 , 2/3, 3/5 , 5/8, 8/13, ……

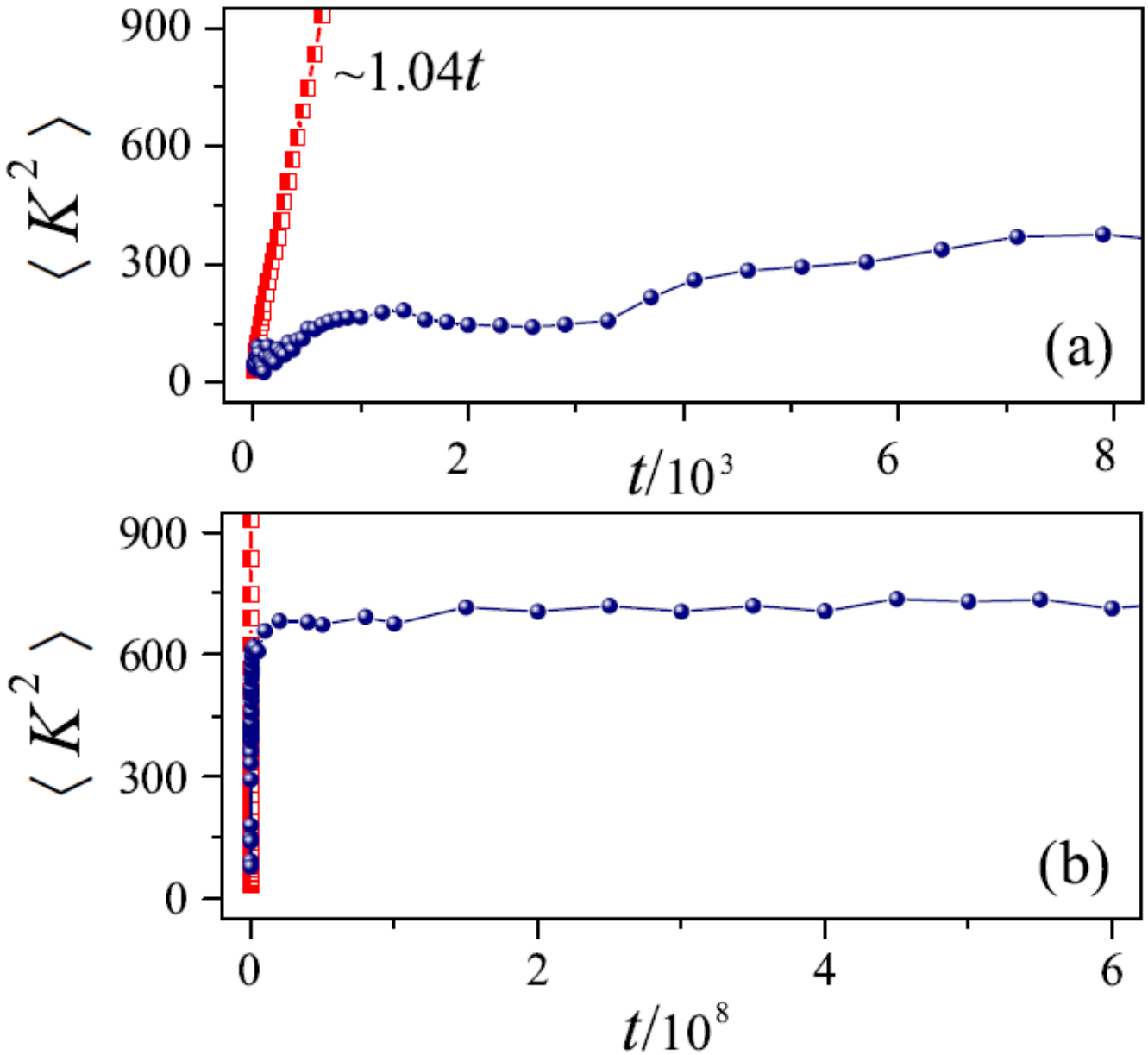
the time is defined as the time up to which the collision sequence of two successive rational approximants, coincide

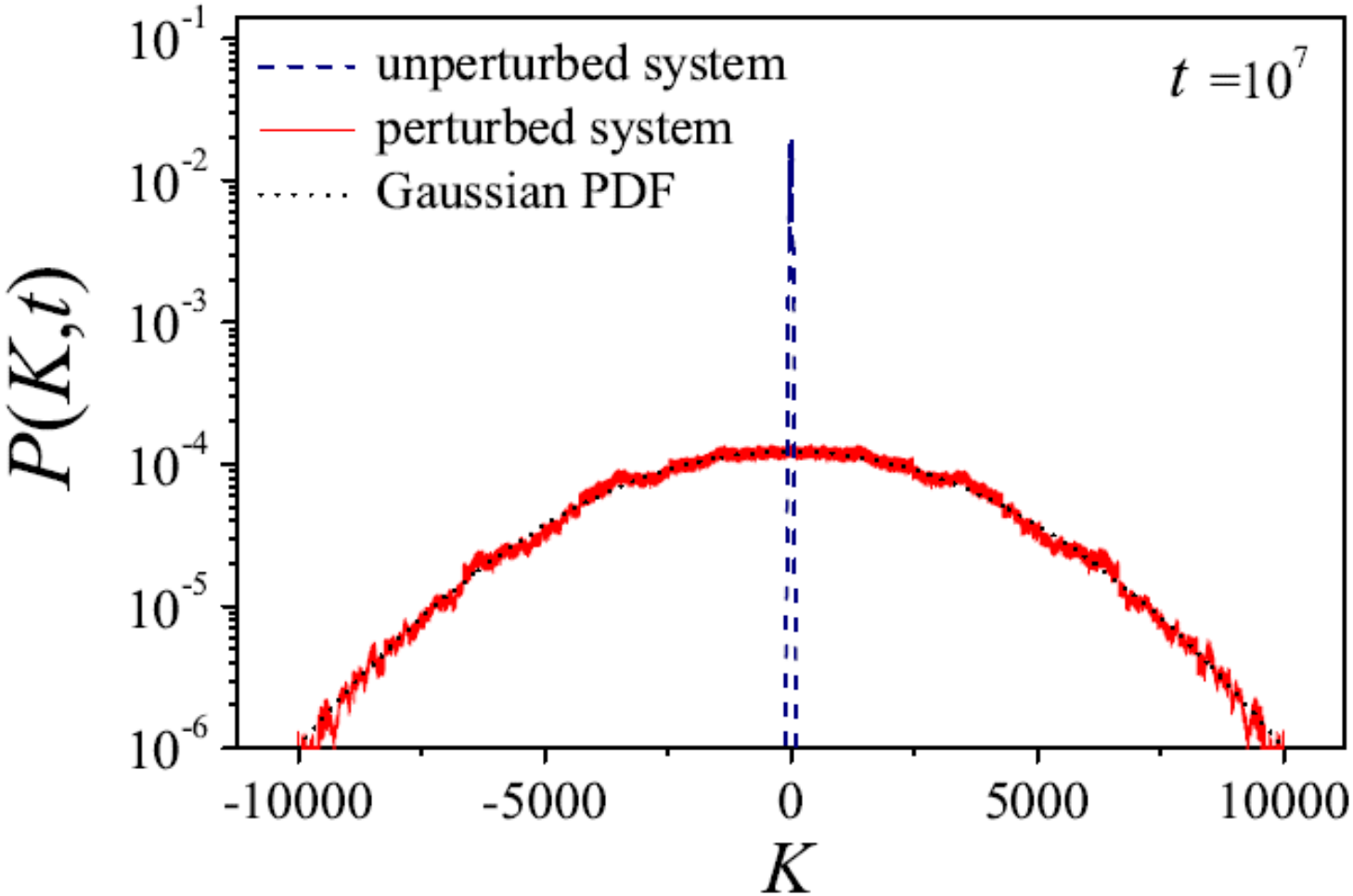


Number of visited K values up to


$t = 10^4$
$t = 10^5$
$t = 10^6$
$t = 10^7$
$t = 10^8$
10^{-2}
10^{-3}
$P(K,t)$
-80
-40
0
40
80
K

The variance of P(K,t)




unperturbed system
perturbed system
Gaussian PDF
$t = 10^7$
$P(K,t)$
K
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
-10000
-5000
0
5000
10000

No stability islands: **orbits are dense on the energy surface but the system is non ergodic.**

Analogy with quantum dynamical localization: the dynamics is determined by number theoretic properties of
(of kicking period)