A two-stage approach to relaxation in locally confined hard sphere systems

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Abstract

I will describe the characterization of heat transfer in models of high-dimensional billiards, which capture the properties of materials that possess both the spatial structure of solids and collisional dynamics of gases. I will discuss the conditions under which the heat conductivity of these models can be universally expressed in terms of the frequency of collisions between gas particles. This universality manifests itself when interactions between gas particles are rare, though not necessarily small. The dynamical properties of these models will be analyzed, and the role of dimensionality emphasized.

Brief Survey

Historical Context

Fourier's law (1822) describes the phenomenological relaxation of heat towards a uniform temperature :

$$\partial_t T(x,t) = \partial_x [\kappa \partial_x T(x,t)]$$

The works of Maxwell (1867) and Boltzmann (1872) on the Kinetic Theory of Gases have emphasized the mechanical origin of heat flow.

The Challenge

Can we provide a derivation of this law from first principles in the framework of Hamiltonian mechanics?

Motivation from Material Science

Aerogels are 99.8% air-filled nano-porous materials which are remarkable thermal insulators. They have the spatial structure of solid materials and their kinetics is similar to rarefied gases.

Solid smoke

- Solid, gaseous and radiative heat conductions are inhibited
- Gas molecules typically collide with the nano-pore walls rather than among themselves
- This provides a local equilibration mechanism

Our Perspective

Because of the confining mechanism of gas molecules

local equilibrium (*without energy exchange*) precedes local thermalisation

Two-stage scenario for local thermalisation

Thermal conduction proceeds over three well-separated time scales :

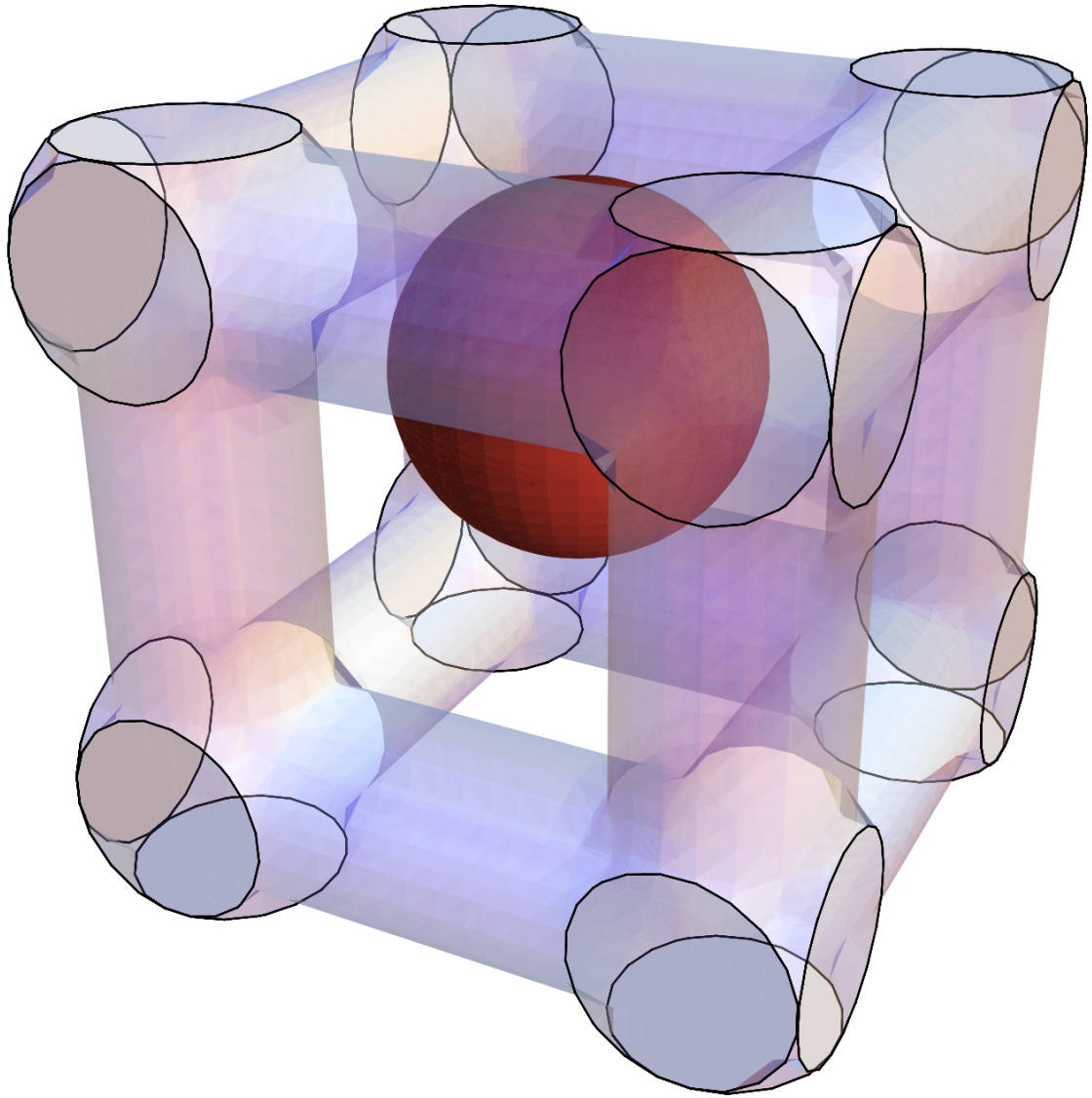
- short time scale τ_{wall}
- intermediate time scale τ_{binary}
- long time scale τ_{macro}

$$\tau_{\text{wall}} \ll \tau_{\text{binary}} \ll \tau_{\text{macro}}$$

This scenario offers the means to deriving Fourier's law!

An idealized aerogel

A one-parameter class of equivalent semi-dispersing billiards



An idealized aerogel

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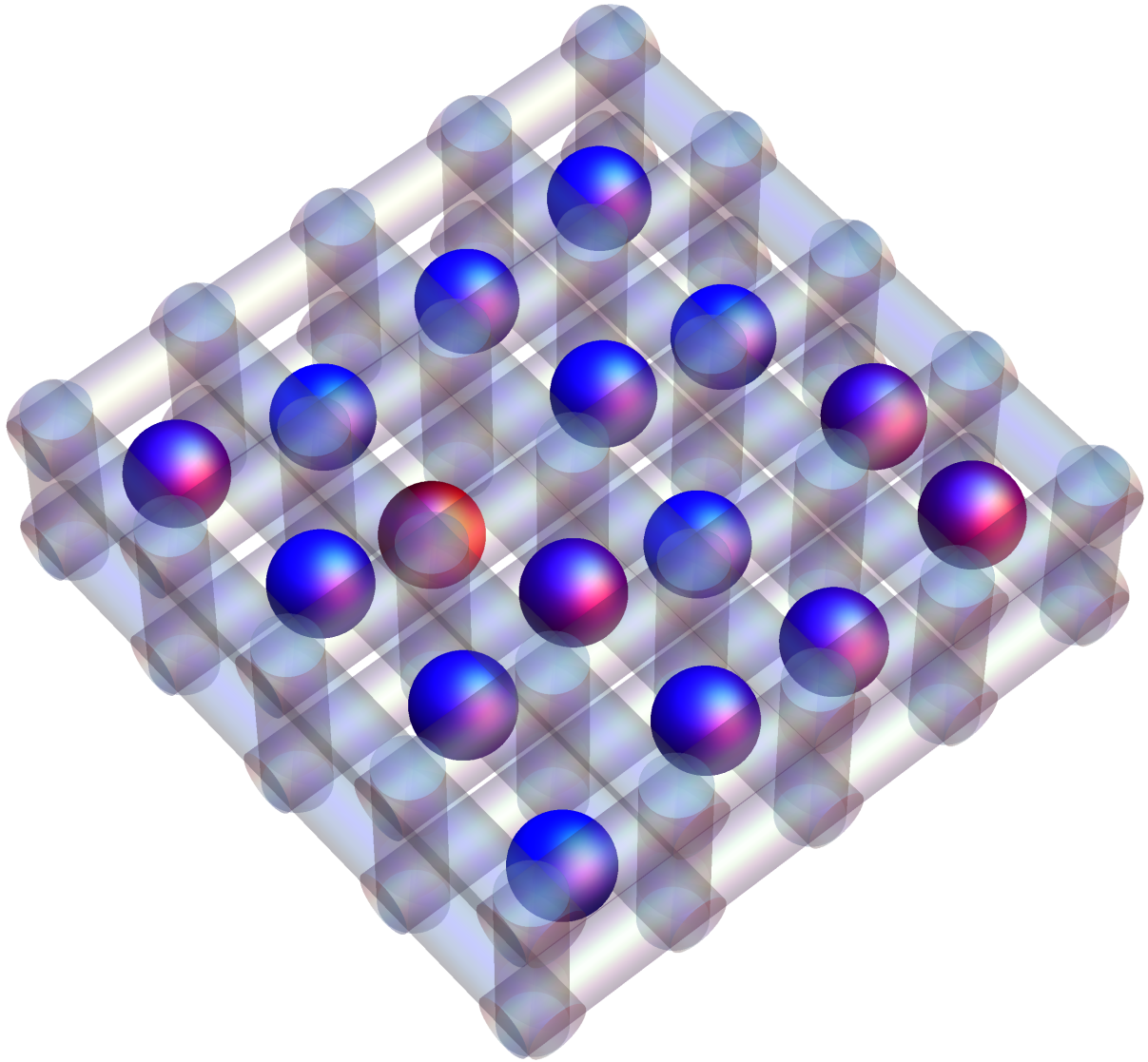
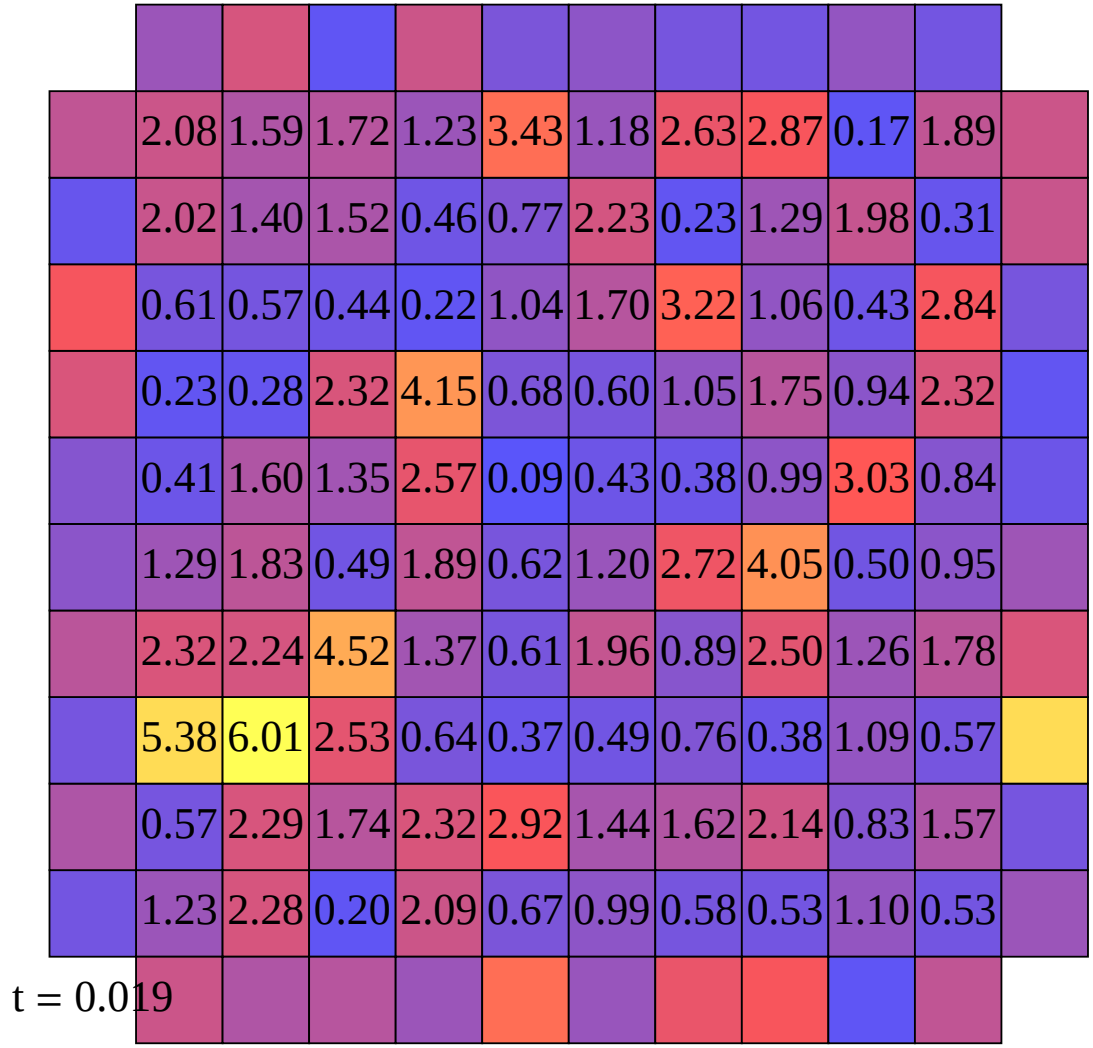


Stochastic Energy Exchanges

P Gaspard and TG J Stat Mech P08020 (2009)



Outline

Sinai billiards as models of mass transport

Models of heat transport with mass confinement

Stochastic reduction by coarse-graining

Thermal conductivity of the mechanical model
- Lattice billiards
- Square-Strings Model

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Mass transport in a periodic Sinai billiard

L A Bunimovich and Ya Sinai Comm. Math. Phys. **78** 247, 479 (1980)
J Machta and R Zwanzig Phys. Rev. Lett. **50** 1959 (1983)

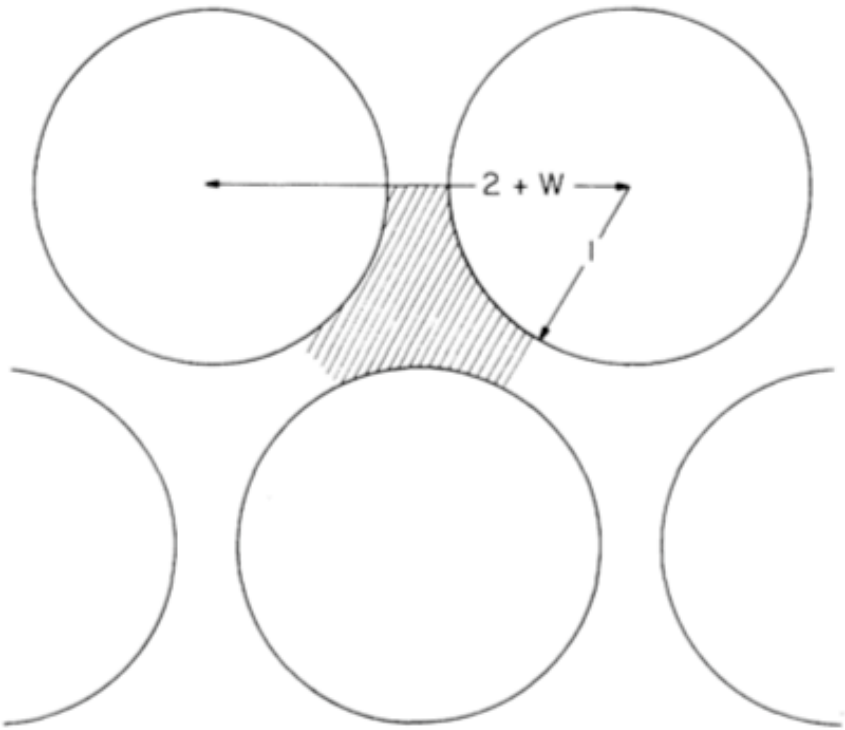
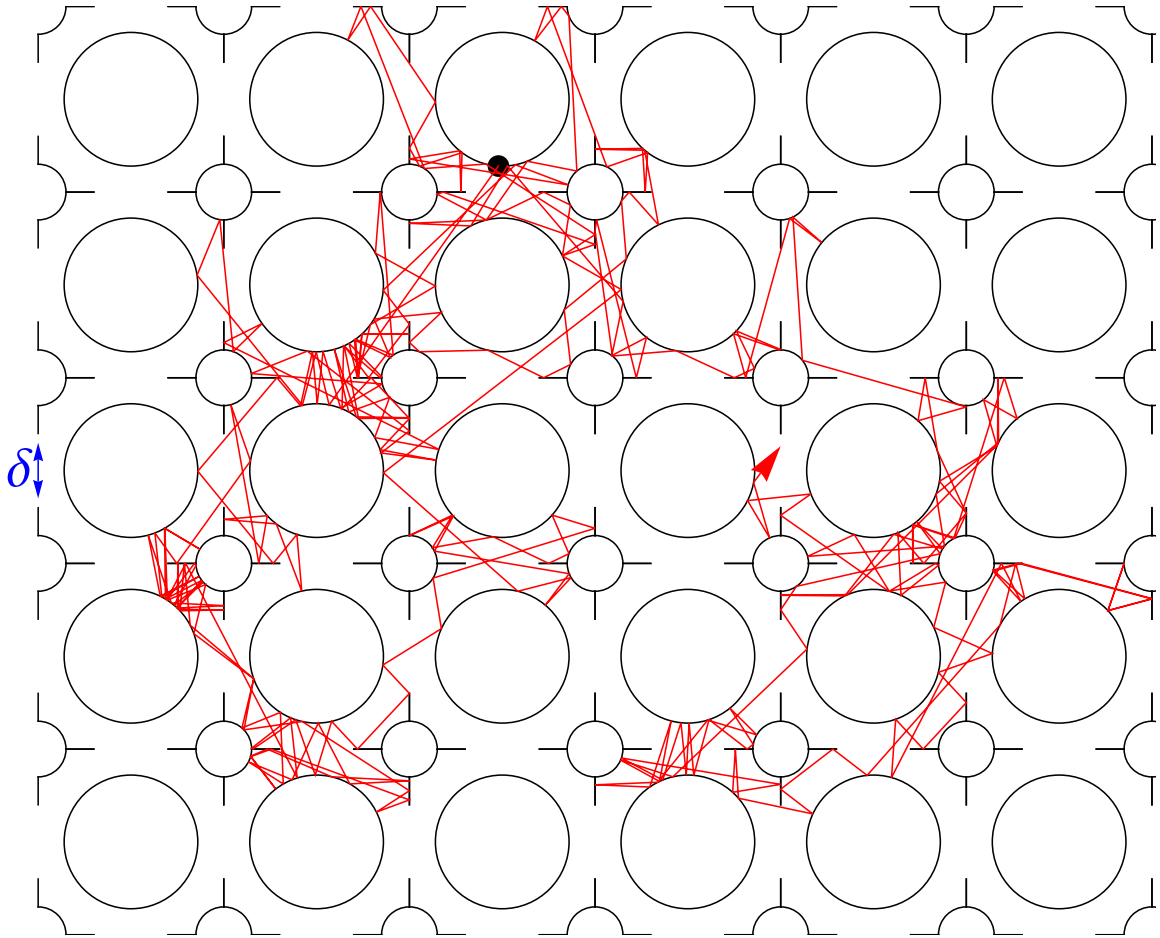


FIG. 1. The geometry of the scatterers in the periodic Lorentz gas. The cross-hatching indicates a single triangular trapping region.

Mass transport in a periodic Sinai billiard

TG and D P Sanders Phys. Rev. E **80** 041121 (2009)
TG and D P Sanders J. Phys. A **43** 5001 (2010)
TG, H C Nguyen and D P Sanders J. Phys. A **44** 065001 (2011)



Diffusive transport at the macroscopic scale

From microscopic to mesoscopic to macroscopic scales

$$p(\mathbf{n}, \mathbf{r}, \mathbf{v}, t) \to p_{\mathrm{leq}}(\mathbf{n}, t) \to P(\mathbf{r}, t)$$

Fokker-Planck equation at macroscopic scale

$$\partial_t P(\mathbf{r}, t) = \mathcal{D} \nabla^2 P(\mathbf{r}, t)$$

with diffusion coefficient

$$\mathcal{D} = \frac{v \delta l^2}{\pi A} = \frac{l^2}{4\tau}$$

This is the Machta Zwanzig approximation

Statistical evolution

pseudo-Liouville equation for $p(\mathbf{n}, \mathbf{r}, \mathbf{v}, t)$

$$\partial_t p = \left\{ -\mathbf{v} \cdot \partial_{\mathbf{r}} + \sum_{n=1}^{c} K^{(d)} + \sum_{j=1}^{4} W^{(j)} \right\} p + \sum_{j=1}^{4} J^{(j)} p$$

where

- $-\mathbf{v} \cdot \partial_{\mathbf{r}}$ is the advection term due to the motion of the particle inside the cell
- the disk collision term $K^{(d)}$ rules the collisions with the fixed discs
- the wall collision term $W^{(j)}$ rules the collisions with the (virtual) flat walls
- the jump term $J^{(j)}$ accounts for the advection of the tracer across the cell boundaries

Continuous-time random walk

Local equilibrium distribution

$$p_{\rm leq}(\mathbf{n},t) = \int \mathrm{d}\tilde{\mathbf{r}} \int \mathrm{d}\tilde{\mathbf{v}} \delta(\tilde{v}^2 - v^2) p(\mathbf{n},\tilde{\mathbf{r}},\tilde{\mathbf{v}},t)$$

changes in time only according to jump events:

$$\partial_t p_{\rm leq}(\mathbf{n},t) = \sum_{j=1}^{4} \int \mathrm{d}\tilde{\mathbf{r}} \int \mathrm{d}\tilde{\mathbf{v}} \delta(\tilde{v}^2 - v^2) J^{(j)} p(\mathbf{n},\tilde{\mathbf{r}},\tilde{\mathbf{v}},t)$$

Jump operator (right wall)

$$\begin{aligned} J^{(1)} p(\mathbf{n},\mathbf{r},\mathbf{v},t) &= v_x \delta(r_x - l/2)\theta(r_y + \delta/2)\theta(\delta/2 - r_y)\theta(v_x) \\ &\quad \times [p(\mathbf{n}+(1,0),\mathbf{r},-v_x,v_y,t) - p(\mathbf{n},\mathbf{r},v_x,v_y,t)] \end{aligned}$$

Continuous-time random walk ct'd

Under the closure approximation

$$p(\mathbf{n}, \tilde{\mathbf{r}}, \tilde{\mathbf{v}}, t) = \frac{1}{\pi A}\delta(\tilde{v}^2 - v^2)p_{\mathrm{leq}}(\mathbf{n}, t)$$

the Liouville equation reduces to a master equation:

$$\partial_t p_{\mathrm{leq}}(\mathbf{n}, t) = \sum_{j=1}^{4} \frac{v\delta}{\pi A}[p_{\mathrm{leq}}(\mathbf{n} + \mathbf{e}_j, t) - p_{\mathrm{leq}}(\mathbf{n}, t)]$$

This is a continuous-time random walk

The waiting-time distribution is exponential with timescale

$$\tau_{\mathrm{J}} = \frac{\pi A}{4v\delta}$$

Diffusion process

The master equation reduces to a Fokker-Planck equation in the continuum limit $\mathbf{r} = l\mathbf{n}$, $l \to 0$, $v \sim l^{-2}$:

$$p_{\mathrm{leq}}(\mathbf{n}, t) \to P(\mathbf{r}, t)$$

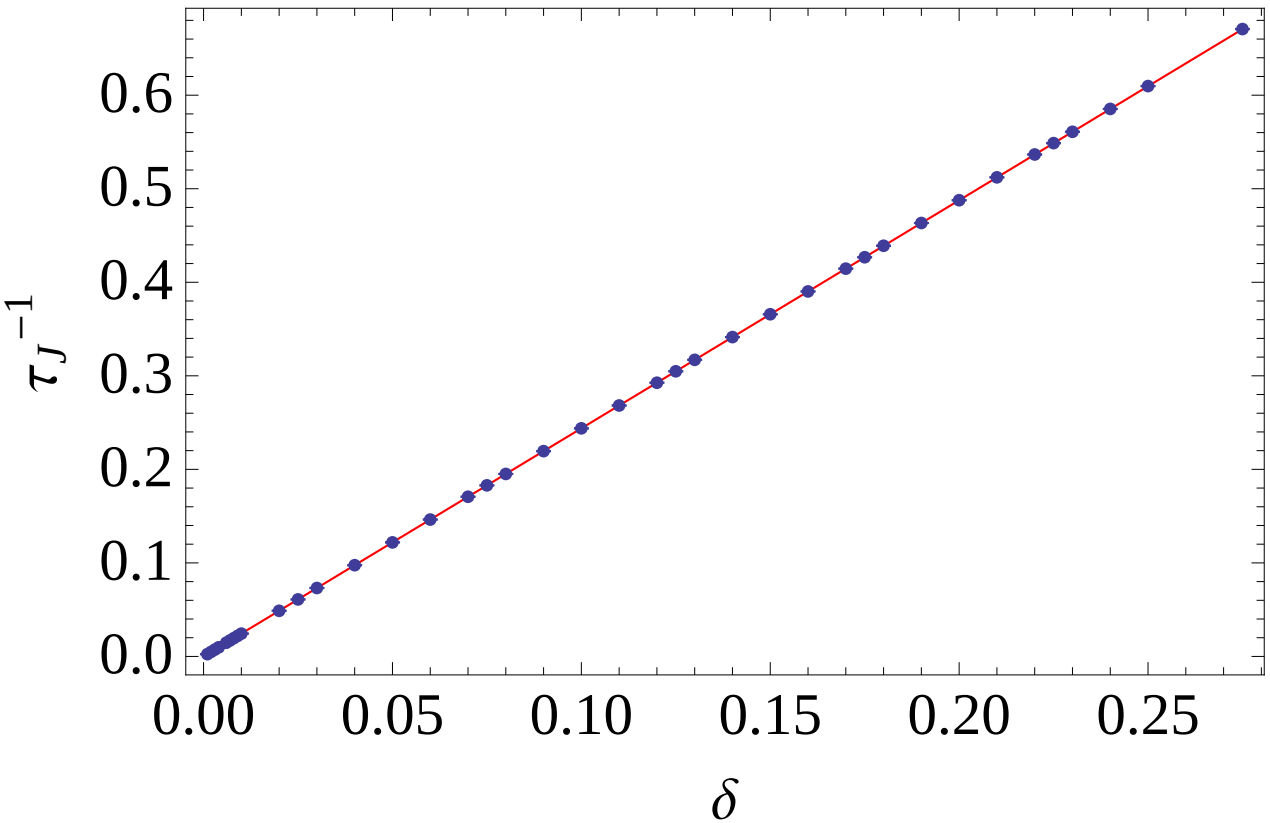
$$\partial_t P(\mathbf{r}, t) = \mathcal{D} \nabla^2 P(\mathbf{r}, t)$$

with the diffusion coefficient

$$\mathcal{D} = \frac{v \delta l^2}{\pi A} = \frac{l^2}{4 \tau_{\mathrm{J}}}$$

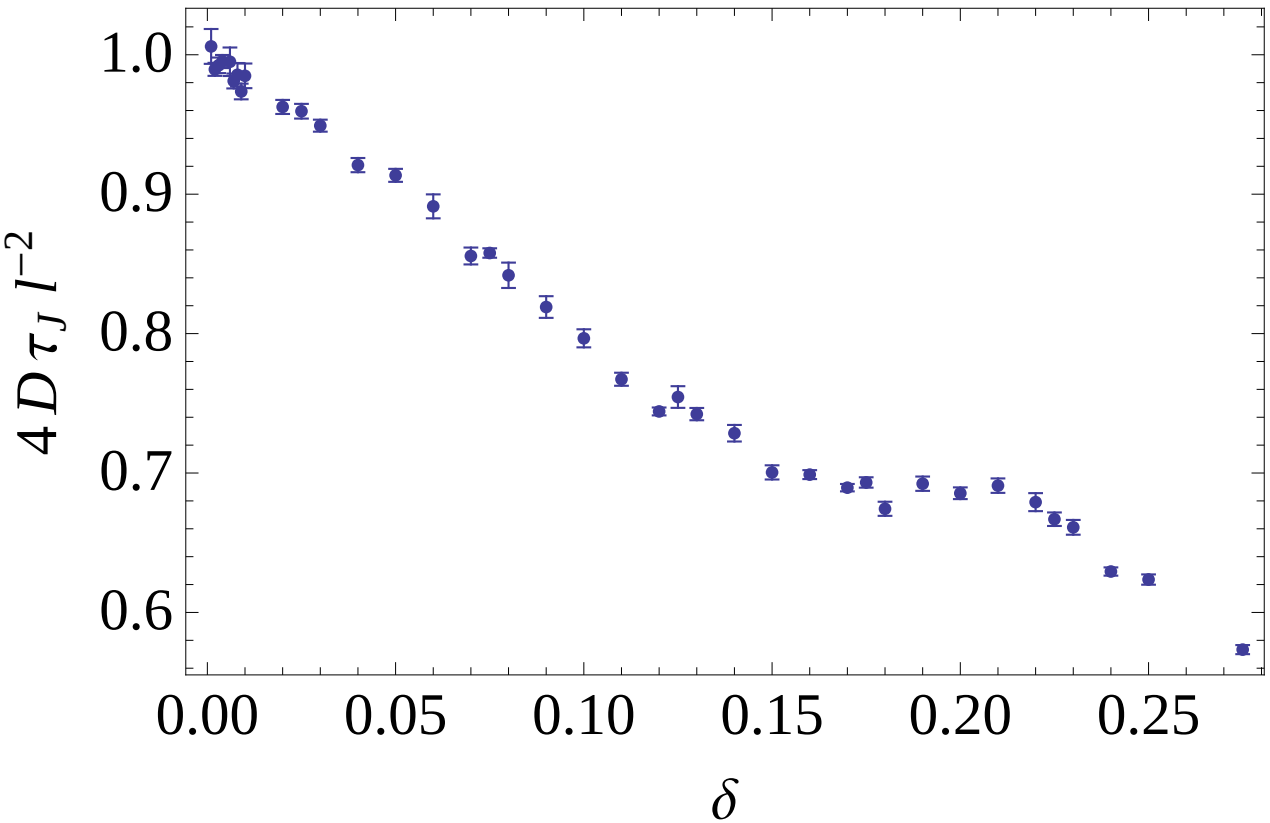
Numerical results for the billiard table

Timescales vs. cell opening parameter



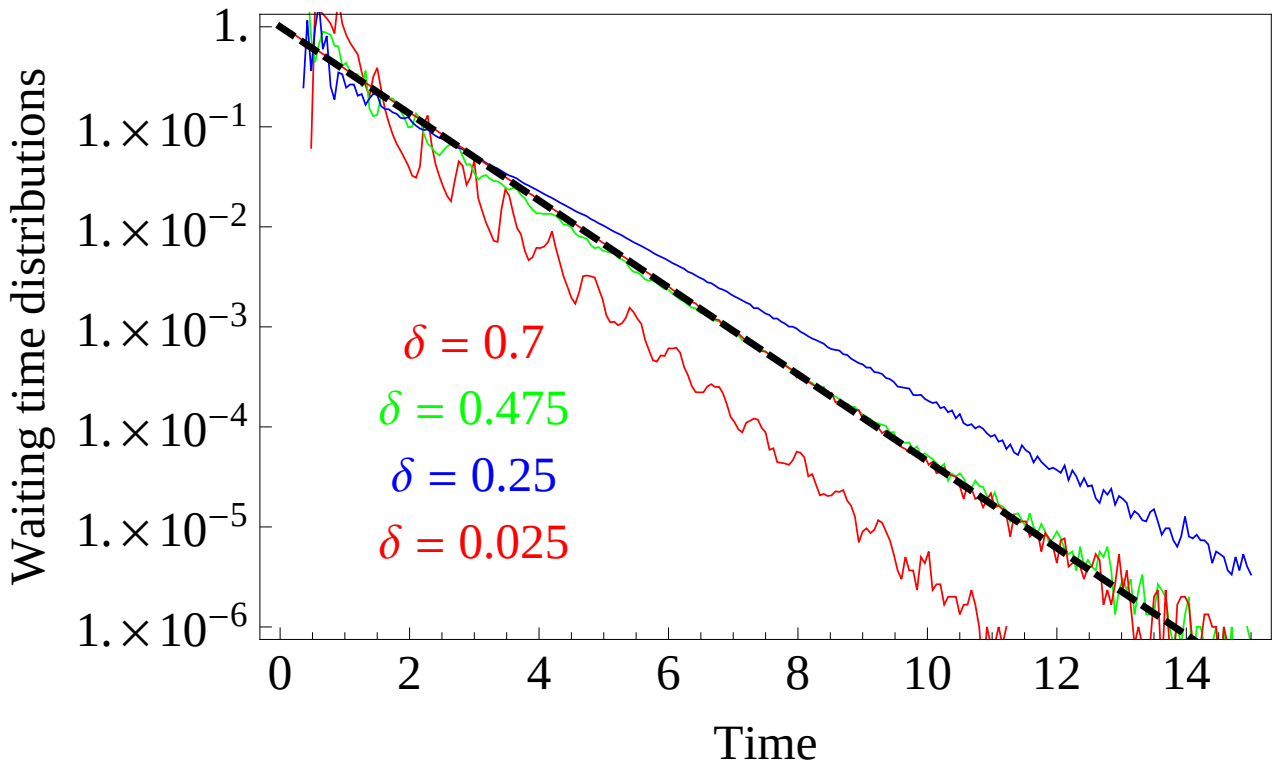
Numerical results for the billiard table

Diffusion coefficient vs. cell opening parameter



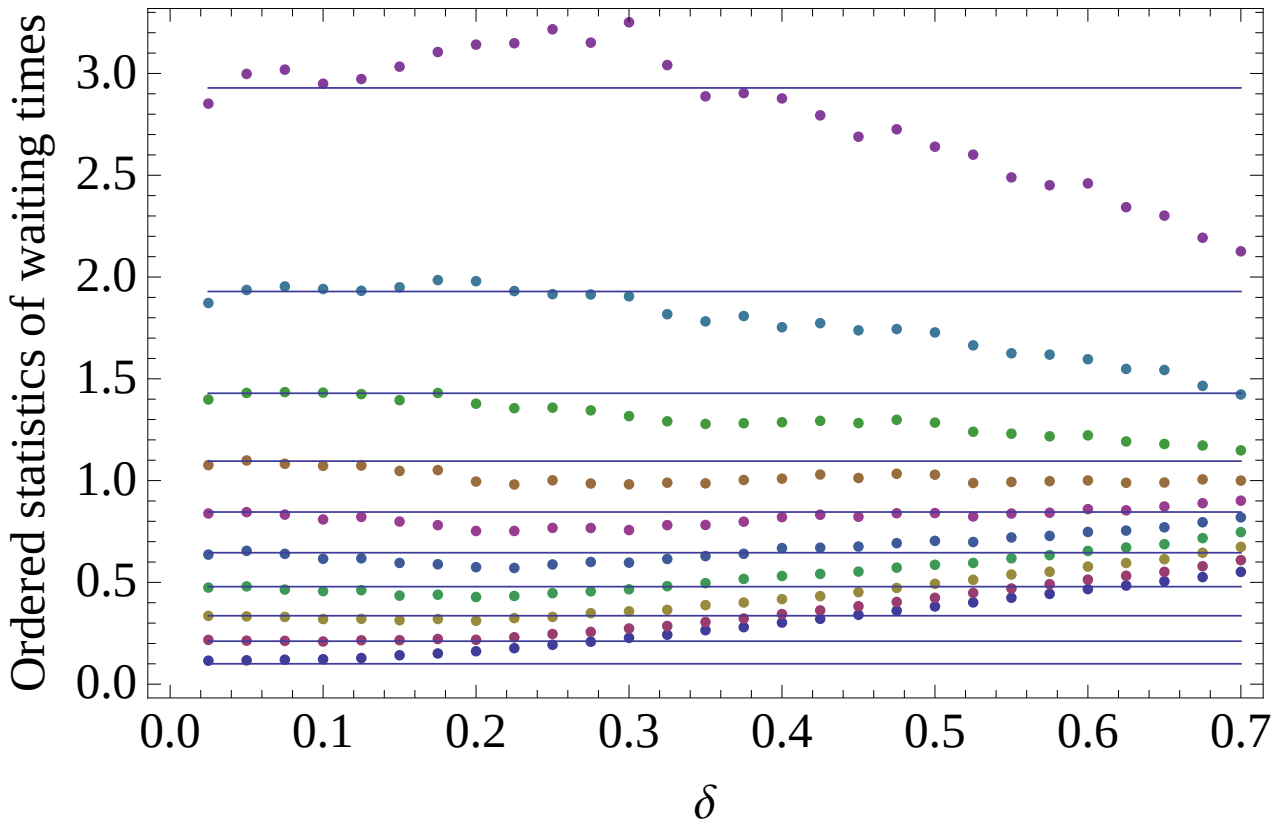
Numerical results for the billiard table

Waiting-time distributions



Numerical results for the billiard table

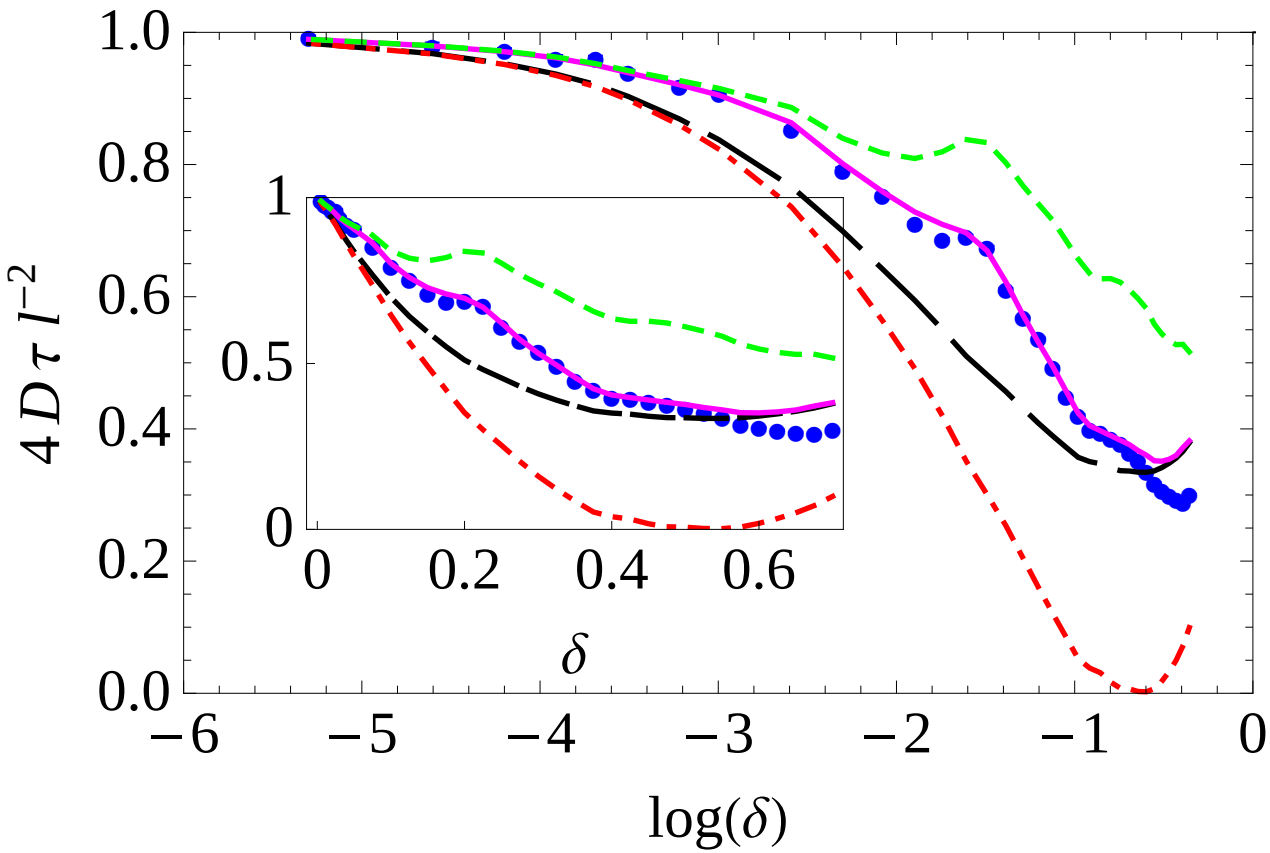
Exponential test of waiting-time distributions



Numerical results for the billiard table

Finite-size corrections due to persistent effects

TG and D P Sanders Phys. Rev. E **80** 041121 (2009)



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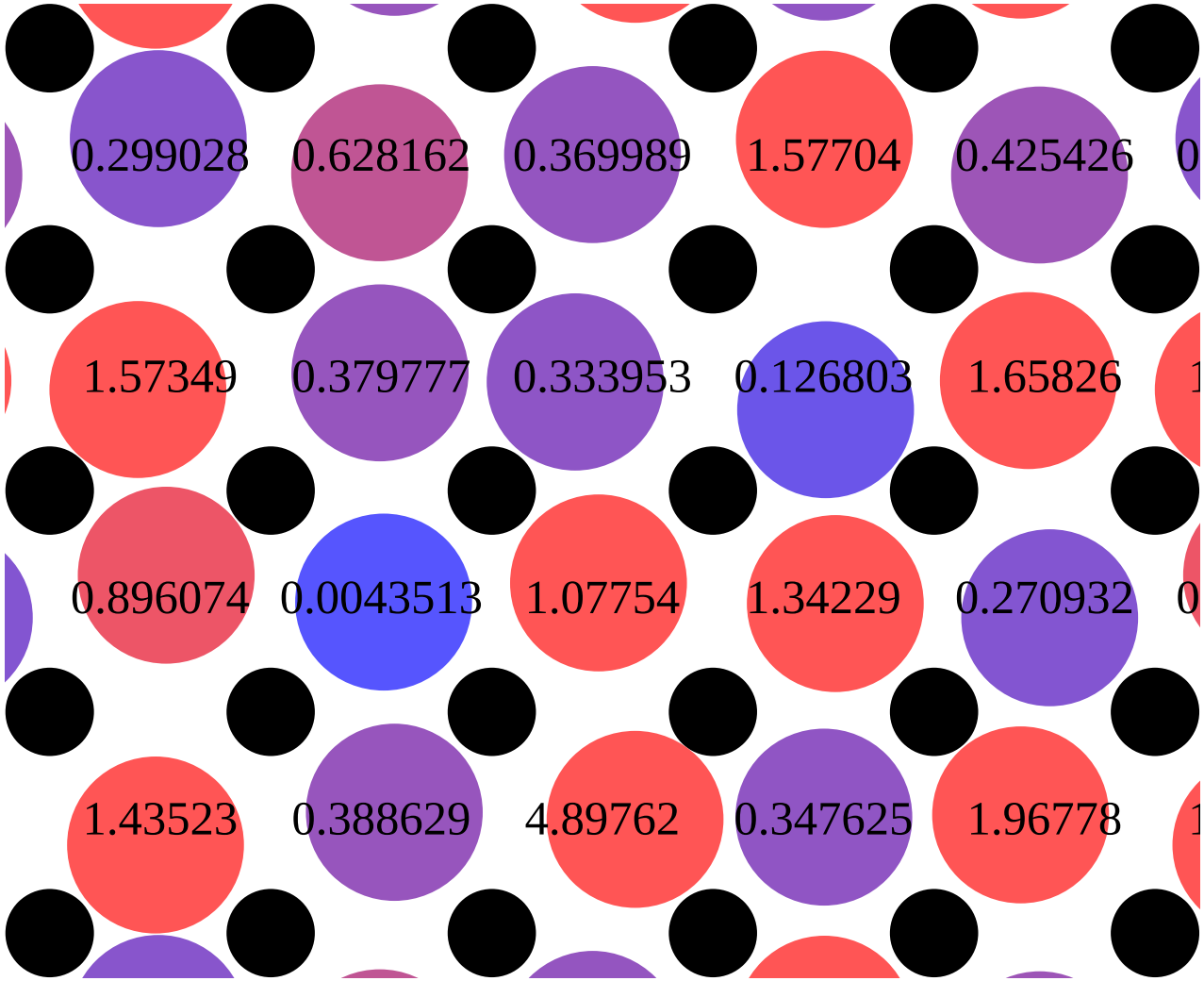
Lattice Billiards: locally confined hard disk gases

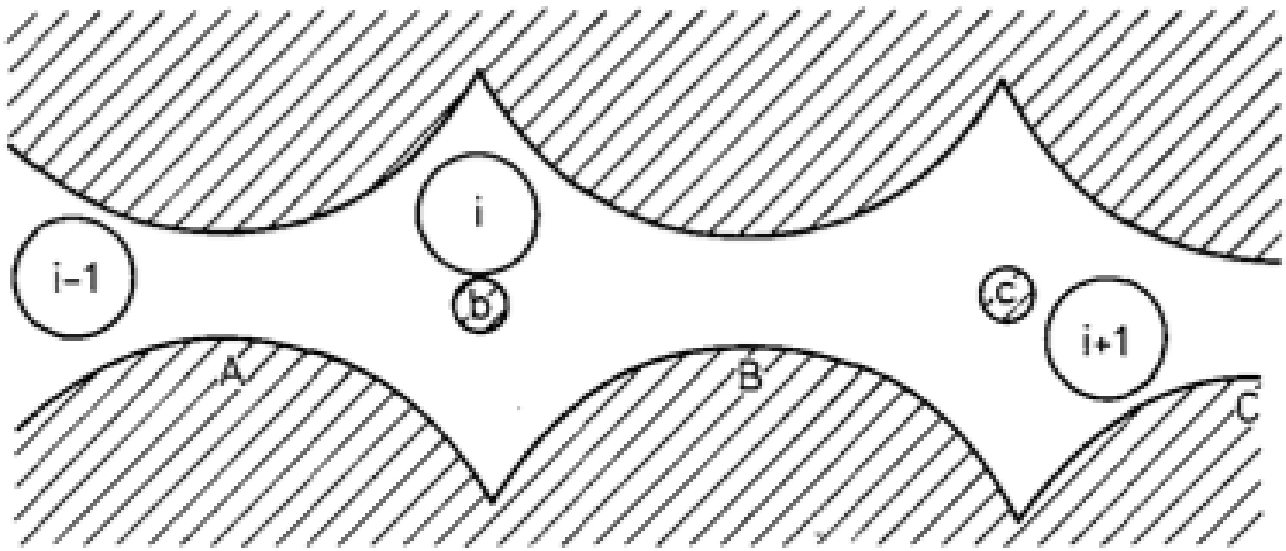
P Gaspard and TG New J Phys **10** 103004 (2008)
P Gaspard and TG Phys Rev Lett **101** 020601 (2008)
Upright Square Geometry, $\rho = 0.60$, $\rho_m = 0.40$



Ergodic systems of *n* balls in a billiard table

L A Bunimovich, C Liverani, A Pellegrinotti and Y Suhov

Commun Math Phys **146** 357 (1992)

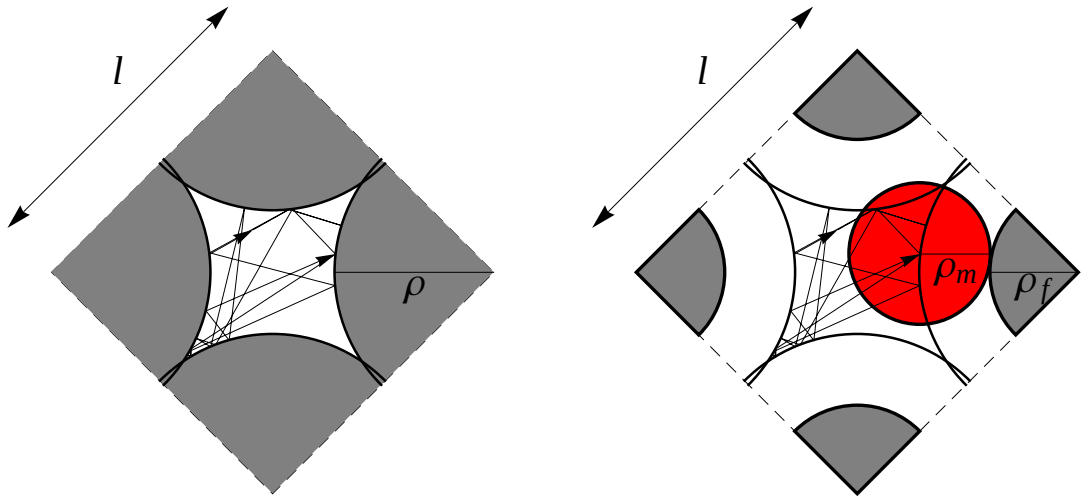


Main Theorem

The dynamical system generated by the motion of any number *n* of adjacent balls in this billiard table is a K-flow on each connected component of a constant energy manifold.

Local Dynamics

Two equivalent representations of a dispersing billiard table:



Two parameters

$$l/2 < \rho < l/\sqrt{2} \text{ and } 0 < \rho_{\mathrm{m}} < \rho \ (\rho = \rho_{\mathrm{m}} + \rho_{\mathrm{f}})$$

Mean free path

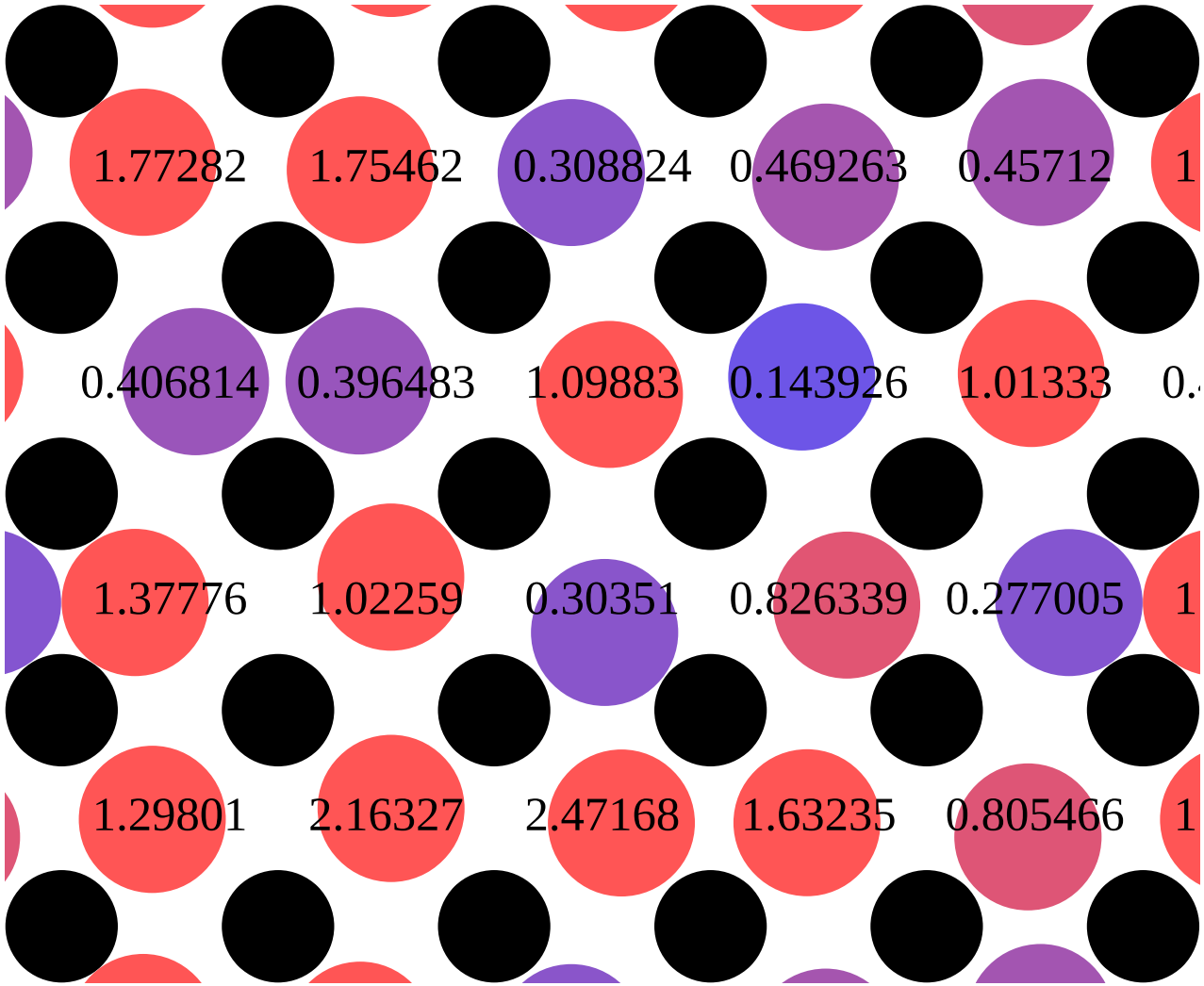
$$\pi|\mathcal{B}_\rho|/|\partial\mathcal{B}_\rho| \propto 1/\nu_{\mathrm{w}}$$

Lattice Billiards – binary collisions dominate

Upright Square Geometry, $\rho = 0.60$, $\rho_m = 0.49$

Lattice Billiards – local dynamics dominates

Upright Square Geometry, $\rho = 0.60$, $\rho_m = 0.34$

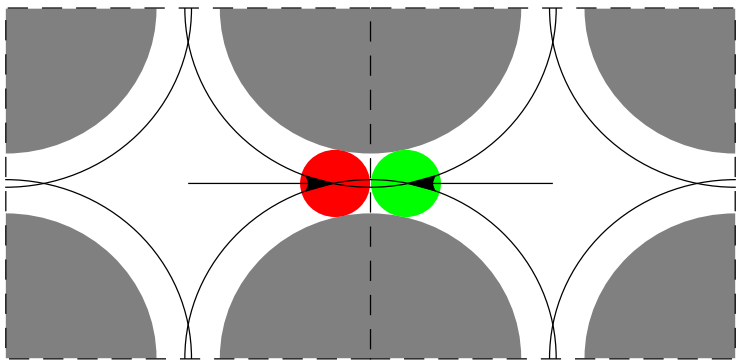


Binary Collisions

Energy exchanges occur when two moving particles located in neighbouring cells collide. These events are possible when

$$\rho_{\mathrm{m}} > \rho_{\mathrm{c}} \equiv \sqrt{\rho^2 - \frac{l^2}{4}}$$

Binary collision event in the critical geometry $\rho_{\mathrm{m}} = \rho_{\mathrm{c}}$



Separation of time scales

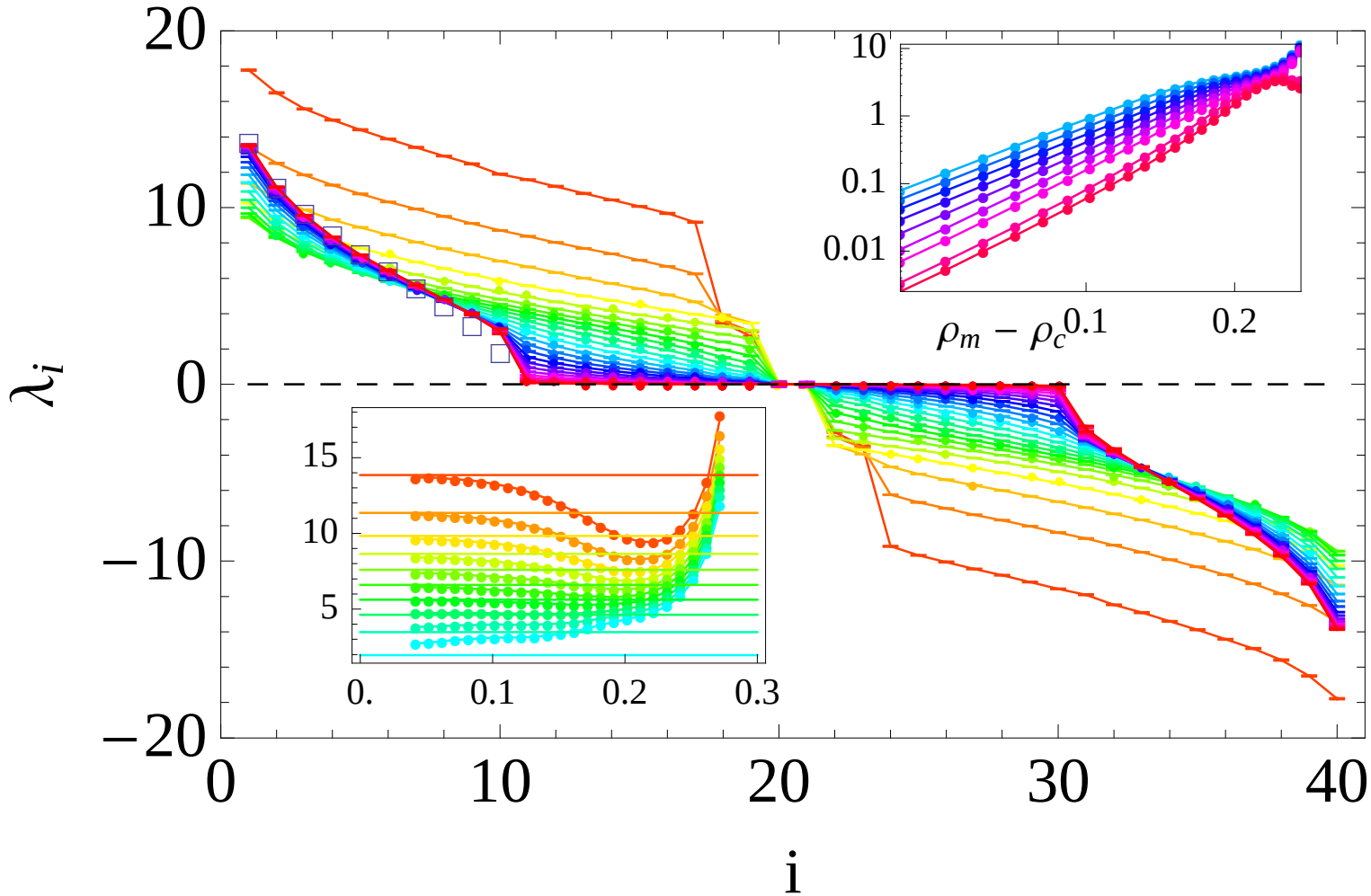
(binary collision frequency) $\nu_{\mathrm{B}} \ll \nu_{\mathrm{w}}$ (wall collision frequency)

Lyapunov Spectrum

Close to the critical geometry, at equilibrium :

$$\lambda_i = \lambda_+ \sqrt{\frac{2k_B T}{m} \left[\ln \frac{N}{i - 1/2} \right]} \qquad i = 1, \ldots, N$$

Lyapunov Spectrum

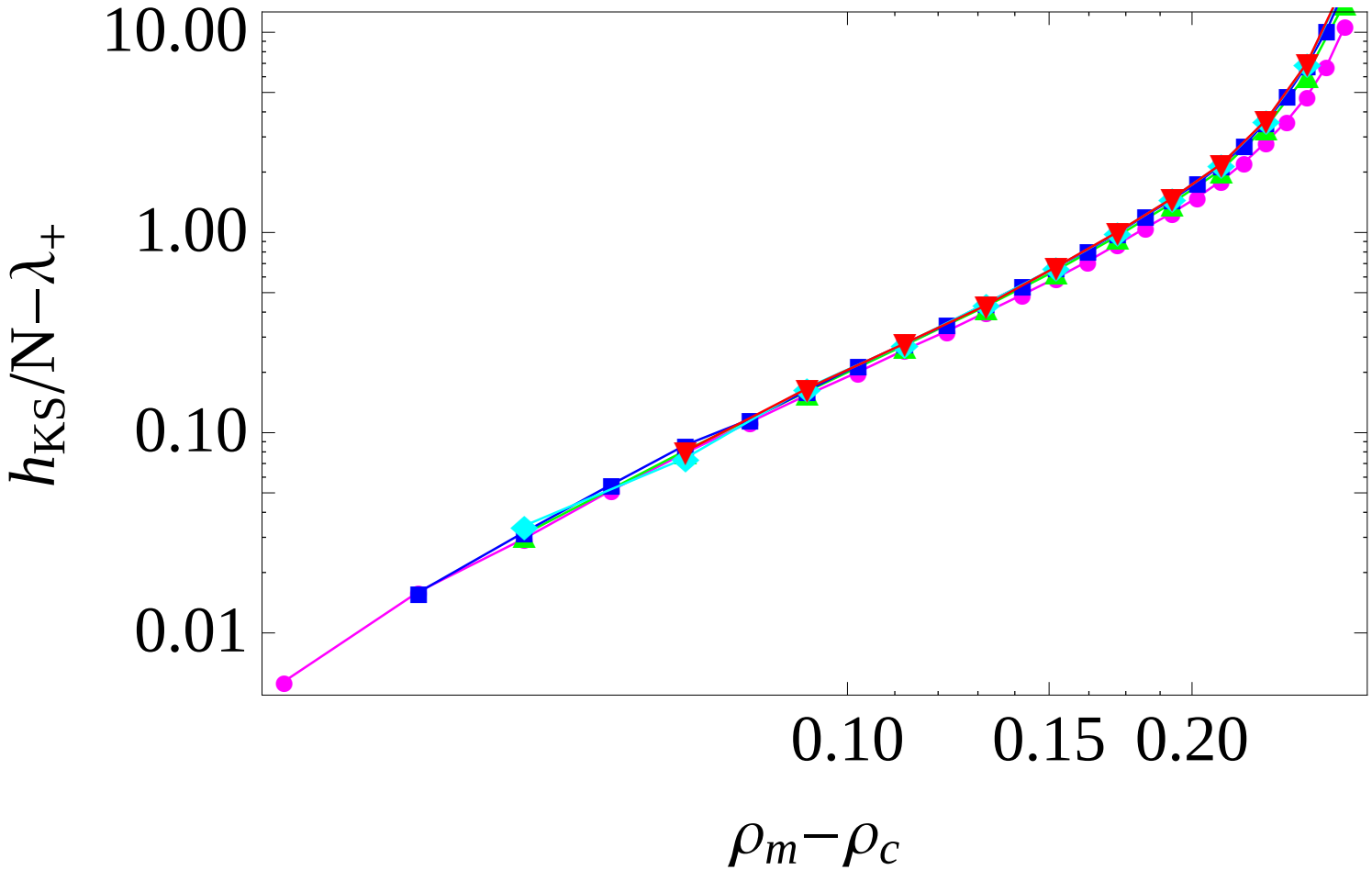


Kolmogorov Sinai Entropy

Close to the critical geometry, at equilibrium :

$$h_{\mathrm{KS}} = \sum_{i=1}^{N} \lambda_i \simeq N\sqrt{\frac{\pi}{4}}\lambda_+$$

Kolmogorov Sinai Entropy



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Kinetic Theory

P Gaspard and TG New J Phys **10** 103004 (2008)

The phase-space probability density $p_N(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N, t)$ evolves according to the pseudo-Liouville equation

$$\partial_t p_N = \sum_{a=1}^{N} \left[-\mathbf{v}_a \cdot \partial_{\mathbf{r}_a} + \sum_{k=1}^{d} K^{(a,k)} \right] p_N + \frac{1}{2} \sum_{a,b=1}^{N} B^{(a,b)} p_N$$

where

- $-\mathbf{v}_a \cdot \partial_{\mathbf{r}_a}$ is the advection term due to the motion of the particle a inside its cell;
- the wall term $K^{(a,k)}$ is the operator ruling the collisions of particle a on the fixed disc k;
- the binary collision term $B^{(a,b)}$ rules the collisions between the particles a and b in neighbouring cells.

From Deterministic to Stochastic Dynamics

The local equilibrium distribution

$$P_N^{(\mathrm{leq})}(\epsilon_1,\ldots,\epsilon_N,t) \equiv \int \prod_{a=1}^{N} \mathrm{d}\mathbf{r}_a \mathrm{d}\mathbf{v}_a p_N(\{\mathbf{r}_i,\mathbf{v}_i\},t) \prod_{a=1}^{N} \delta(\epsilon_a - m v_a^2/2)$$

is left unchanged by the advection and wall terms.

We can make a closure approximation to obtain the time-evolution of the local equilibrium distribution

$$\partial_t P_N^{(\mathrm{leq})}(\epsilon_1,\ldots,\epsilon_N,t) =$$
$$\frac{1}{2}\sum_{a,b=1}^{N} \int d\eta \Big[W(\epsilon_a+\eta,\epsilon_b-\eta|\epsilon_a,\epsilon_b)\; P_N^{(\mathrm{leq})}(.,\epsilon_a+\eta,.,\epsilon_b-\eta,.,t)$$
$$- W(\epsilon_a,\epsilon_b|\epsilon_a-\eta,\epsilon_b+\eta)\; P_N^{(\mathrm{leq})}(\ldots,\epsilon_a,\ldots,\epsilon_b,\ldots,t)\Big]$$

Transition Rates (2D dynamics)

The transition rate of the binary collisions of energy transfer η between the neighbouring particles *a* and *b* is given by

$$W(\epsilon_a, \epsilon_b | \epsilon_a - \eta, \epsilon_b + \eta) = \frac{2\rho_{\mathrm{m}} m^2}{(2\pi)^2 |\mathcal{L}_{\rho,\rho_{\mathrm{m}}}(2)|} \int \mathrm{d}\phi \, \mathrm{d}\mathbf{R} \int_{\hat{\mathbf{e}}_{ab}\cdot\mathbf{v}_{ab}>0} \mathrm{d}\mathbf{v}_a \mathrm{d}\mathbf{v}_b \, \hat{\mathbf{e}}_{ab} \cdot \mathbf{v}_{ab} \times \delta\left(\epsilon_a - \frac{m}{2} v_a^2\right) \delta\left(\epsilon_b - \frac{m}{2} v_b^2\right) \times \delta\left(\eta - \frac{m}{2}[(\hat{\mathbf{e}}_{ab} \cdot \mathbf{v}_a)^2 - (\hat{\mathbf{e}}_{ab} \cdot \mathbf{v}_b)^2]\right)$$

where the volume $|\mathcal{L}_{\rho,\rho_{\mathrm{m}}}(2)| \simeq |\mathcal{B}_\rho|^2$, ϕ is the angle of the unit vector $\hat{\mathbf{e}}_{ab}$ connecting *a* and *b*, and $\mathbf{R}$ their center of mass.

Transition Rates (2D dynamics)

After proper time renormalization, the kernel can be written in terms of Jacobi elliptic functions K ($\epsilon_b > \epsilon_a$):

$$W(\epsilon_a, \epsilon_b | \epsilon_a - \eta, \epsilon_b + \eta) =$$

$$\sqrt{\frac{2}{\pi^3}} \times \begin{cases} \sqrt{\frac{1}{\epsilon_a}} K\left(\frac{\epsilon_b+\eta}{\epsilon_a}\right) & -\epsilon_b < \eta < \epsilon_a - \epsilon_b \\ \sqrt{\frac{1}{\epsilon_b+\eta}} K\left(\frac{\epsilon_a}{\epsilon_b+\eta}\right) & \epsilon_a - \epsilon_b < \eta < 0 \\ \sqrt{\frac{1}{\epsilon_b}} K\left(\frac{\epsilon_a-\eta}{\epsilon_b}\right) & 0 < \eta < \epsilon_a \end{cases}$$

Transition Rates (3D dynamics)

P Gaspard and TG J Stat Mech P08020 (2009)

For the underlying 3D hard sphere dynamics, we obtain a simpler kernel:

$$W(\epsilon_a, \epsilon_b | \epsilon_a - \eta, \epsilon_b + \eta) =$$

$$\sqrt{\frac{\pi}{8}} \times \begin{cases} \sqrt{\frac{\epsilon_b+\eta}{\epsilon_a \epsilon_b}} & -\epsilon_b < \eta < \min(\epsilon_a - \epsilon_b, 0) \\ \frac{1}{\sqrt{\max(\epsilon_a, \epsilon_b)}} & \min(\epsilon_a - \epsilon_b, 0) < \eta < \max(\epsilon_a - \epsilon_b, 0) \\ \sqrt{\frac{\epsilon_a-\eta}{\epsilon_a \epsilon_b}} & \max(\epsilon_a - \epsilon_b, 0) < \eta < \epsilon_a \end{cases}$$

Energy Exchange Frequency

Assume a global microcanonical equilibrium at energy $E = \epsilon_1 + \cdots + \epsilon_N$. The energy exchange frequency is

$$\nu_B = \int \mathrm{d}\epsilon \mathrm{d}\epsilon' \mathrm{d}\eta W(\epsilon, \epsilon' | \epsilon - \eta, \epsilon' + \eta) P^{(\mathrm{eq})}_{a,b}(\epsilon, \epsilon')$$

The two-particle energy distribution is

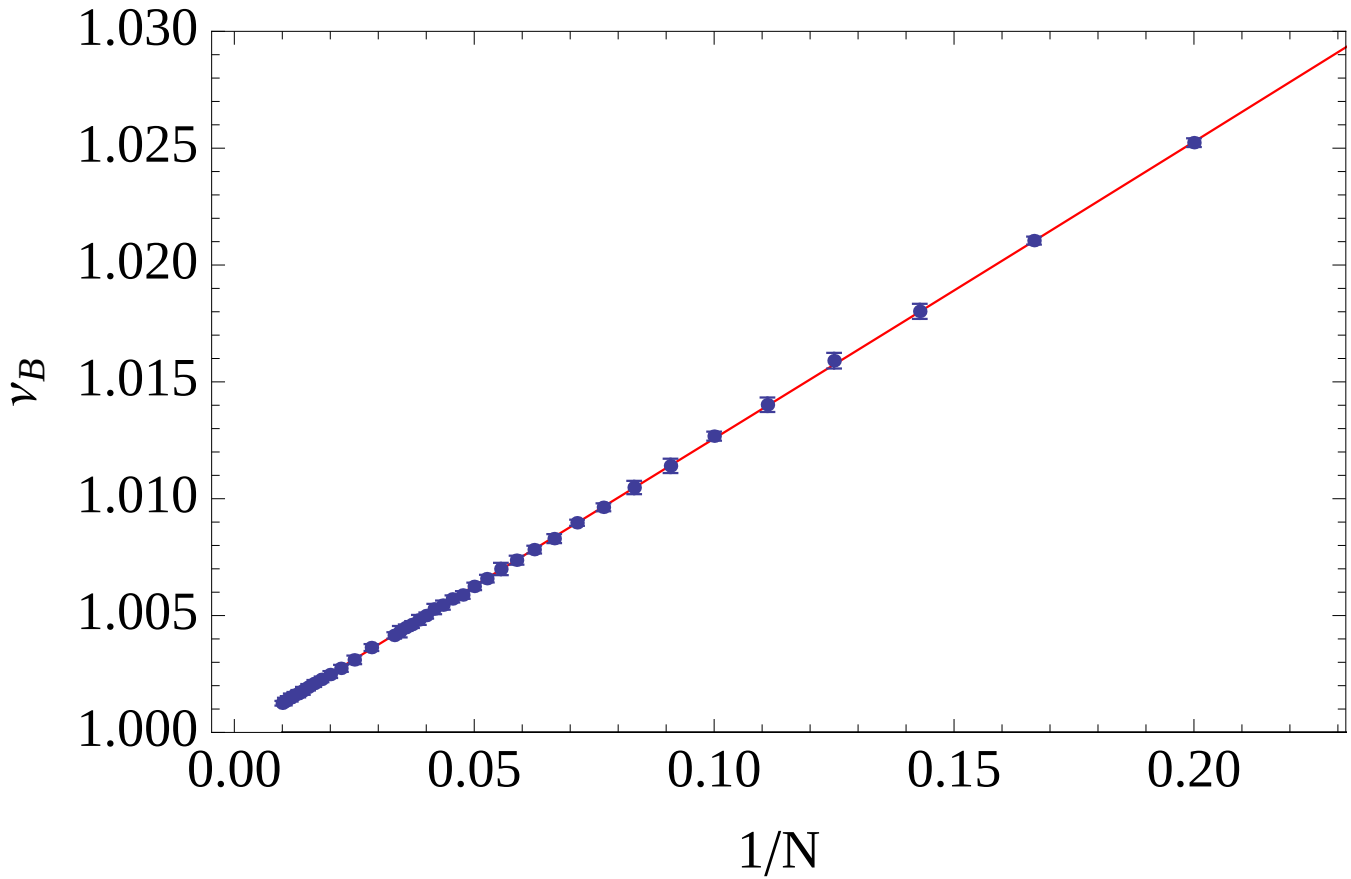
$$P^{(\mathrm{eq})}_{a,b}(\epsilon, \epsilon') = \frac{(N-1)(N-2)}{E^2} \left(1 - \frac{\epsilon + \epsilon'}{E}\right)^{N-3}$$

In the large N limit and letting $E = NT$

$$\nu_B \simeq \sqrt{T}[1 + \mathcal{O}(N^{-1})]$$

Energy Exchange Frequency ct'd

P Gaspard and TG J Stat Mech P11021 (2008)



Energy Diffusion

Helfand moment

$$H(t) = \sum_{a=1}^{N} a\epsilon_a(t)$$

$$\begin{aligned}
\kappa &= \lim_{N\to\infty} \frac{1}{N(E/N)^2} \lim_{n\to\infty} \left\langle \frac{1}{2\tau_n} \Delta H(\tau_n)^2 \right\rangle_{E/N} \\
&= \lim_{N\to\infty} \frac{1}{NT^2} \lim_{n\to\infty} \left[\sum_{i=1}^{n} \left\langle \frac{1}{2\tau_n} \eta(\epsilon_{k_i}, \epsilon_{k_i+1})^2 \right\rangle_T \right. \\
&\quad \left. + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \left\langle \frac{1}{2\tau_n} \eta(\epsilon_{k_i}, \epsilon_{k_i+1}) \eta(\epsilon_{k_j}, \epsilon_{k_j+1}) \right\rangle_T \right]
\end{aligned}$$

Energy Diffusion ct'd

Only static correlations contribute (not trivial!)

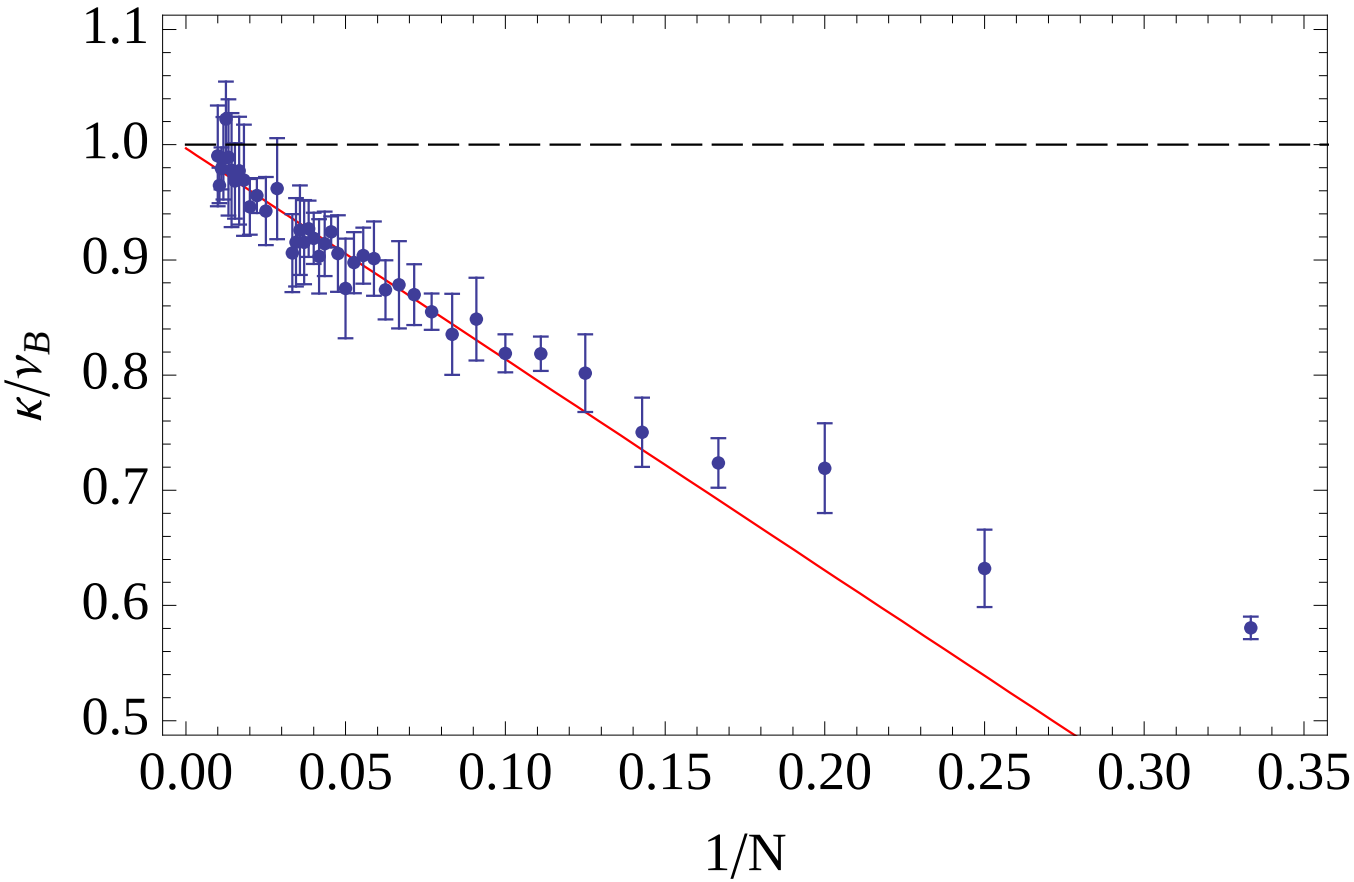
$$\lim_{N\to\infty} \frac{1}{NT^2} \lim_{n\to\infty} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \left\langle \frac{1}{2\tau_n} \eta(\epsilon_{k_i}, \epsilon_{k_i+1}) \eta(\epsilon_{k_j}, \epsilon_{k_j+1}) \right\rangle_T = 0$$

Therefore

$$\kappa = \nu_{\mathrm{B}} = \sqrt{T}$$

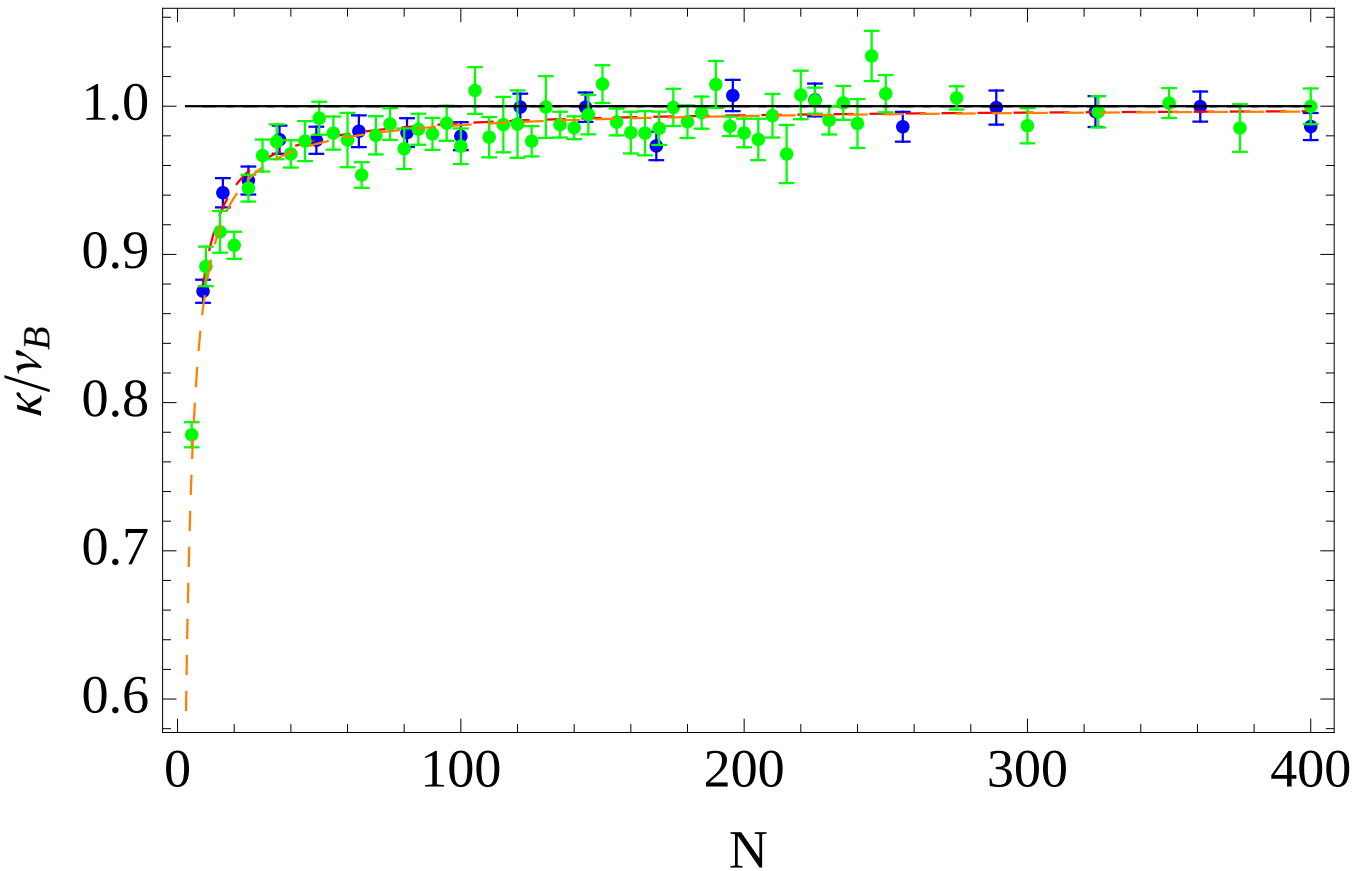
Energy Diffusion for the 2D dynamics

P Gaspard and TG J Stat Mech P11021 (2008)



Energy Diffusion for the 3D dynamics

P Gaspard and TG J Stat Mech P08020 (2009)



Energy Transport

Heat current

$$J_{a,b} = I \int \mathrm{d}\epsilon \mathrm{d}\epsilon' \mathrm{d}\eta\, \eta\, W(\epsilon, \epsilon' | \epsilon - \eta, \epsilon' + \eta) P_{a,b}^{(\mathrm{leq})}(\epsilon, \epsilon', t)$$

Local temperatures

$$T_a(t) = \int \mathrm{d}\epsilon\, \epsilon\, P_a^{(\mathrm{leq})}(\epsilon, t)$$

Fourier's law ($T_a \approx T_b$)

$$J_{a,b} = \frac{\kappa}{I}[T_a(t) - T_b(t)]$$

Non-equilibrium stationary state

Boundary conditions

$$P_{\pm N/2}(\epsilon) = \frac{1}{T_\pm} \exp\left(-\frac{\epsilon}{T_\pm}\right)$$

The one-site distribution obeys a Boltzmann-Kac equation

$$P_a(\epsilon) = \frac{1}{T_a} \exp\left(-\frac{\epsilon}{T_a}\right)$$

is a “quasi” stationary state:

$$\partial_t P_a(\epsilon, t) = \mathcal{O}(\delta T^2)$$

provided $\delta T = \frac{T_+ - T_-}{N} \ll 1$

NESS from solving the BBGKY hierarchy

Does the two-site distribution factorize?

$$P_{a,b}(\epsilon, \epsilon') \stackrel{?}{=} P_a(\epsilon)\, P_b(\epsilon')$$

No, because the current does not have the gradient form!

$$j(\epsilon, \epsilon') \neq \beta \int \mathrm{d}\epsilon'' e^{-\beta\epsilon''} j(\epsilon, \epsilon'') - \beta \int \mathrm{d}\epsilon'' e^{-\beta\epsilon''} j(\epsilon', \epsilon'')$$

NESS from solving the BBGKY hierarchy

The two-site distribution includes a $\mathcal{O}(\delta T)$ correction

$$P_{a,b}(\epsilon, \epsilon') = P_a(\epsilon)\, P_b(\epsilon') + \mathcal{O}(\delta T)$$

This correction does not affect the value of the current!

$$P_{a,b}(\epsilon, \epsilon') = P_a(\epsilon)\, P_b(\epsilon') + \frac{\delta\beta}{\beta} Q_{a,b}(\beta\epsilon, \beta\epsilon')$$

The second order correction correction in the cluster expansion Q is found to be a symmetric function of its arguments

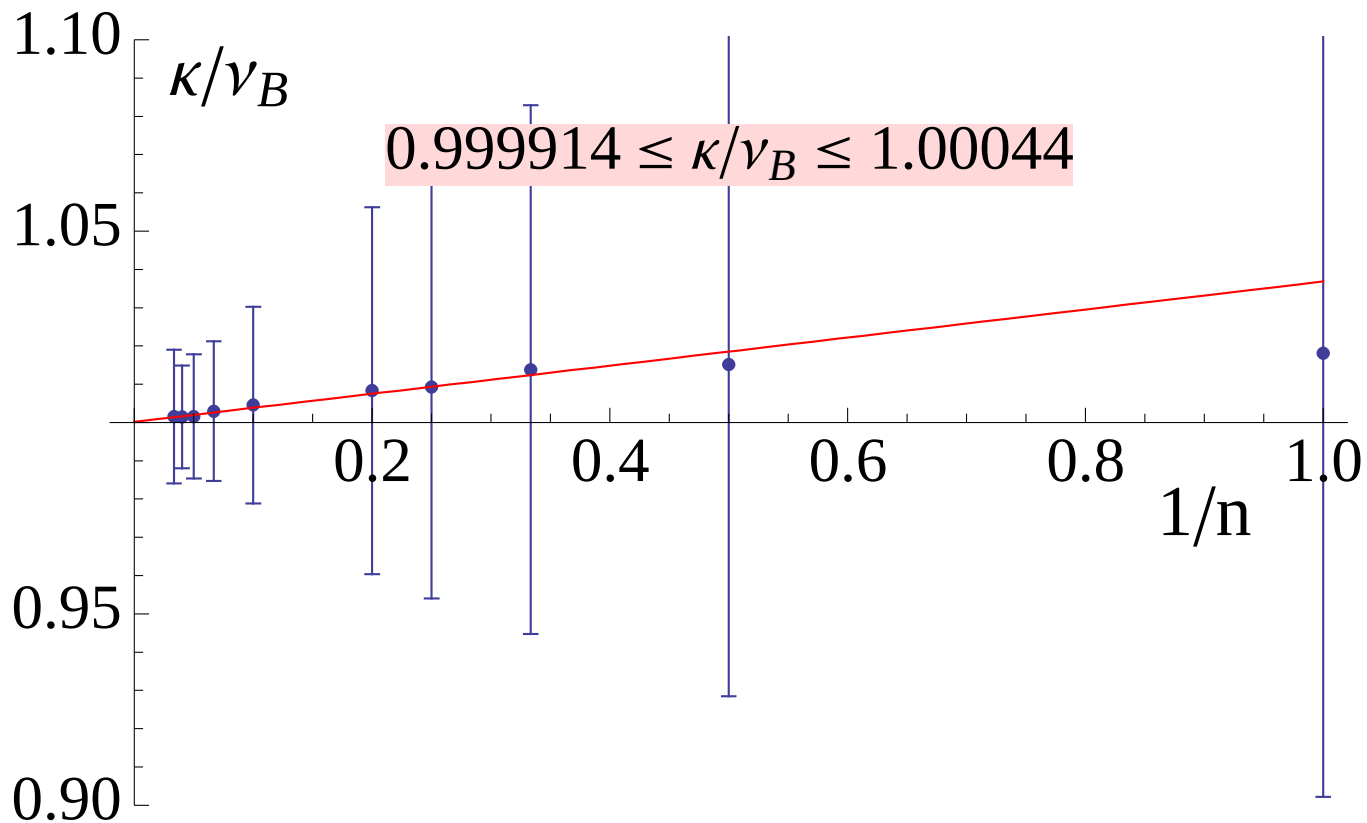
Thermal Conductivity

The linear transport law yields

$$\begin{aligned}\frac{\kappa}{l^2} &= \frac{1}{2(T)^4}\int \mathrm{d}\epsilon_a \mathrm{d}\epsilon_b \mathrm{d}\eta\, \eta(\epsilon_b-\epsilon_a) W(\epsilon_a,\epsilon_b|\epsilon_a-\eta,\epsilon_b+\eta) \\ &\quad \times \exp[-(\epsilon_a+\epsilon_b)/(T)] \\ &= \sqrt{T} \\ &= \nu_{\mathrm{B}}\end{aligned}$$

Thermal conductivity for the 2D dynamics

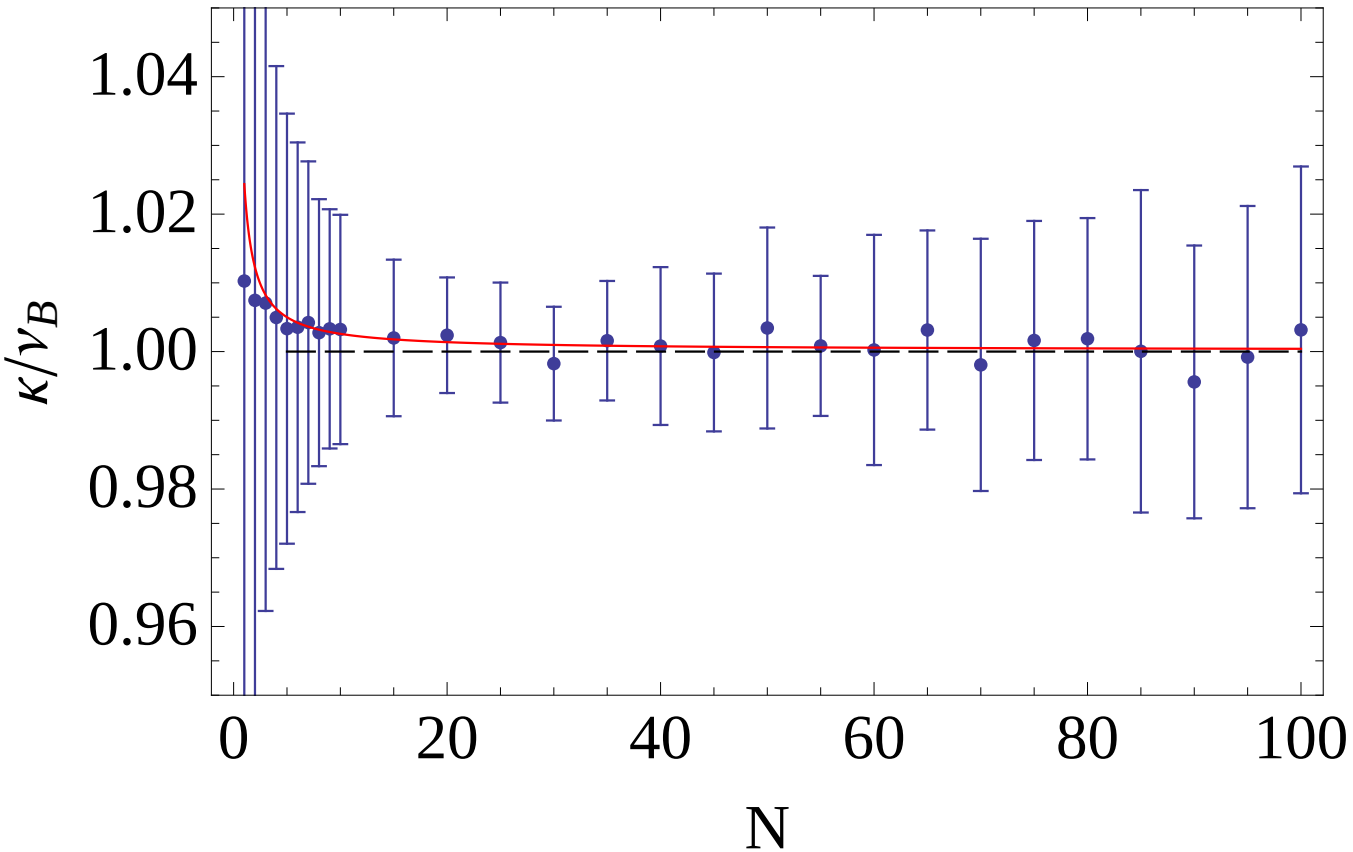
P Gaspard and TG J Stat Mech P11021 (2008)



$(T_- = 0.9,\ T_+ = 1.1)$

Thermal conductivity for the 3D dynamics

P Gaspard and TG J Stat Mech P08020 (2009)



$(T_- = 0.5,\ T_+ = 1.5,\ \kappa/\nu_{\rm B} = 1.0002 \pm 5\,10^{-4})$

Outline

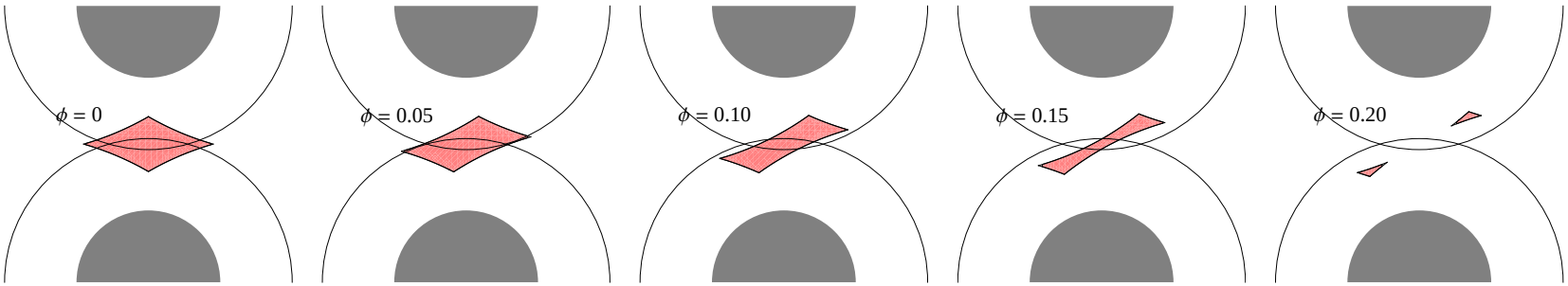
Sinai billiards as models of mass transport

Models of heat transport with mass confinement

Stochastic reduction by coarse-graining

Thermal conductivity of the mechanical model
- Lattice billiards
- Square-Strings Model

Binary Collision Volume



$$\int \mathrm{d}\phi\, \mathrm{d}\mathbf{R} = \frac{128\rho_c}{3l^2}(\rho_m - \rho_c)^3 + \frac{256\rho_c^2}{3l^4}(\rho_m - \rho_c)^4 + \cdots$$

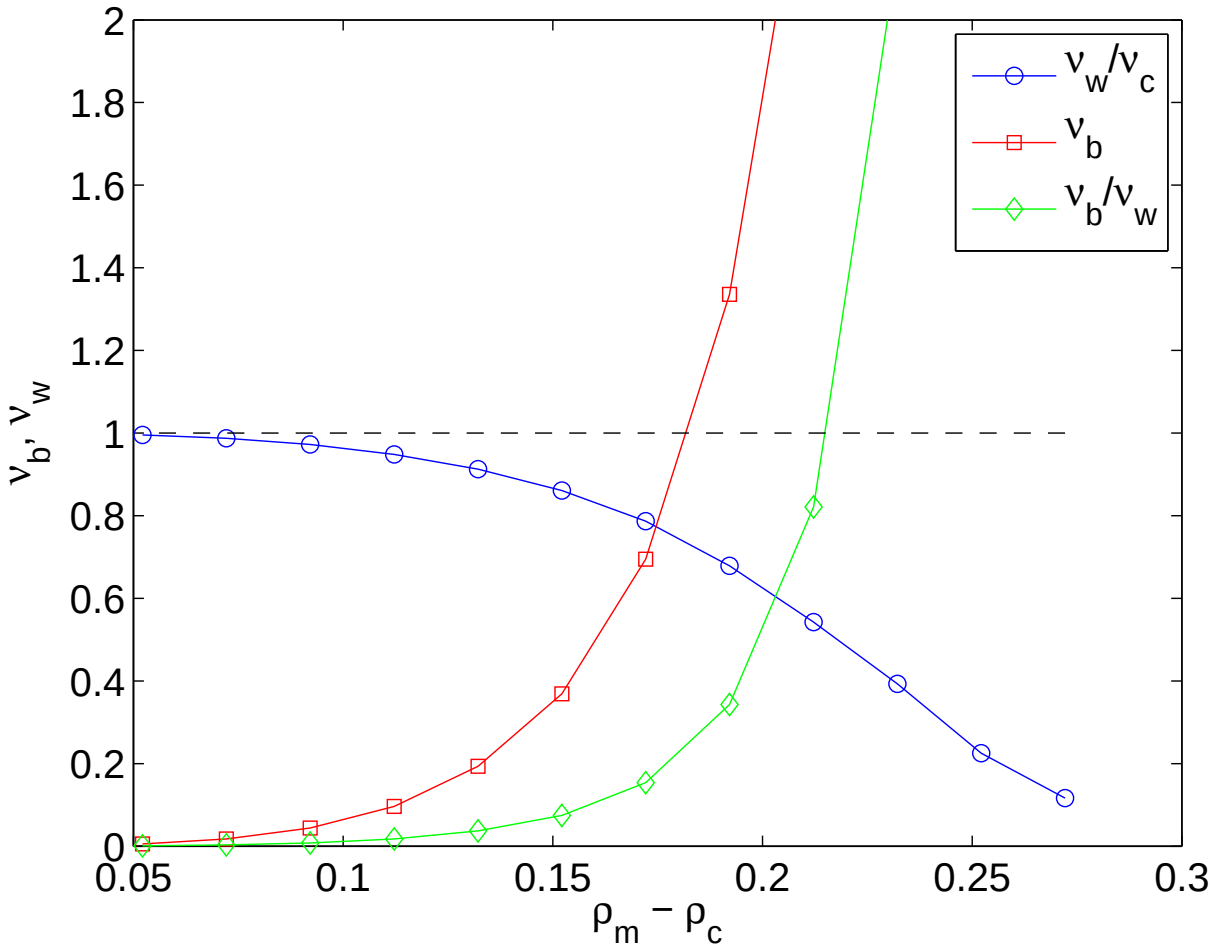
Exact result at the critical geometry

$$\lim_{\rho_m \to \rho_c} \frac{\kappa/l^2}{(\rho_m - \rho_c)^3} = \lim_{\rho_m \to \rho_c} \frac{\nu_B}{(\rho_m - \rho_c)^3} = \frac{2\rho_m}{|\mathcal{B}_\rho|^2}\sqrt{\frac{k_B T}{\pi m}}\frac{128\rho_c}{3l^2}$$

Numerical Results – Lattice Billiard

P Gaspard and TG New J Phys **10** 103004 (2008)

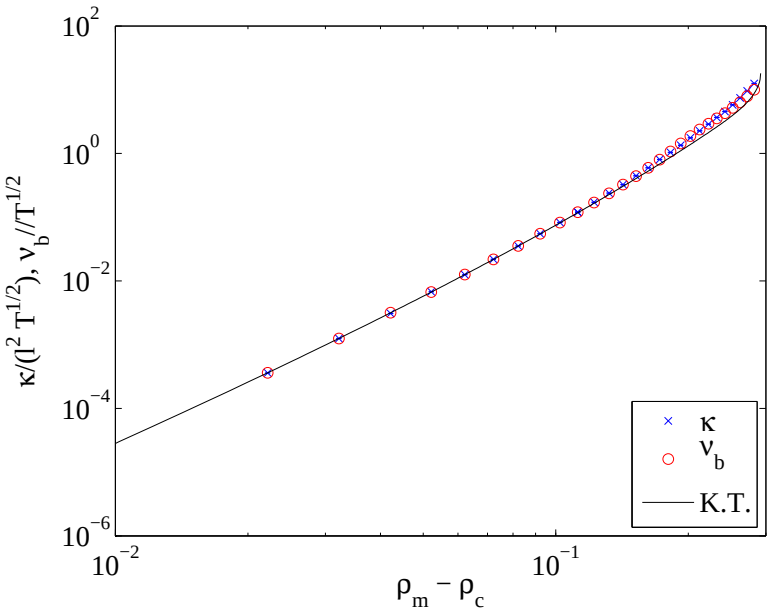
Comparison between the wall and binary collision frequencies

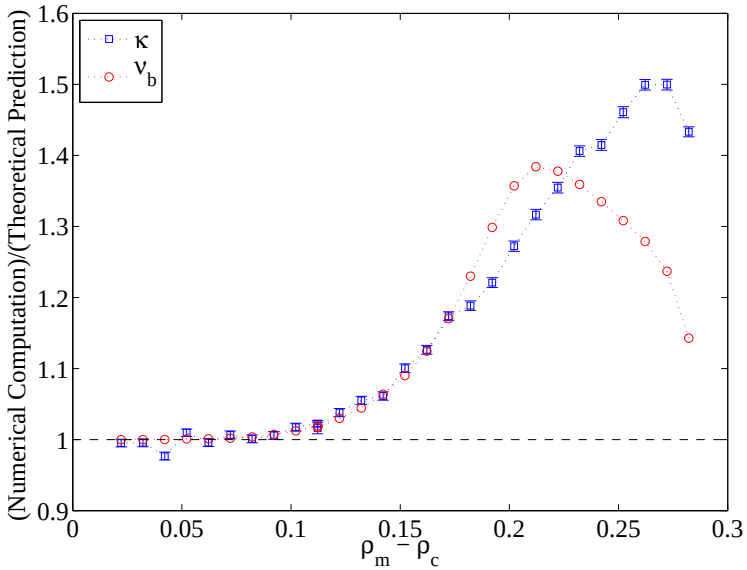


$(\rho = 0.36)$

Numerical Results – Lattice Billiard

Comparison between κ, ν_B and the results of kinetic theory for a single thermalised cell

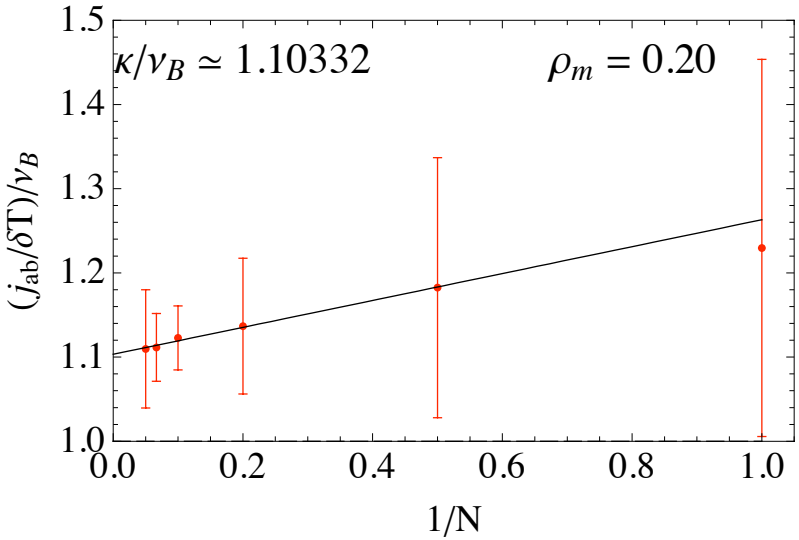


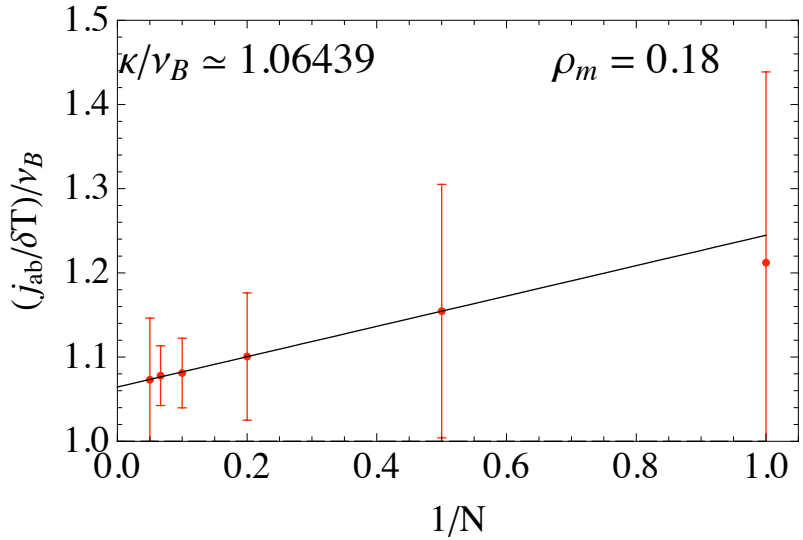


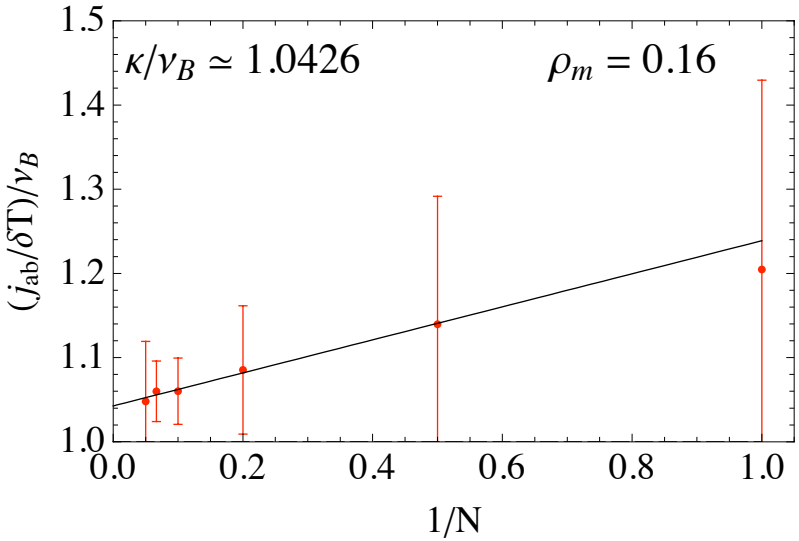
($N = 1$ with stochastic thermalisation, $\rho = 0.36$)

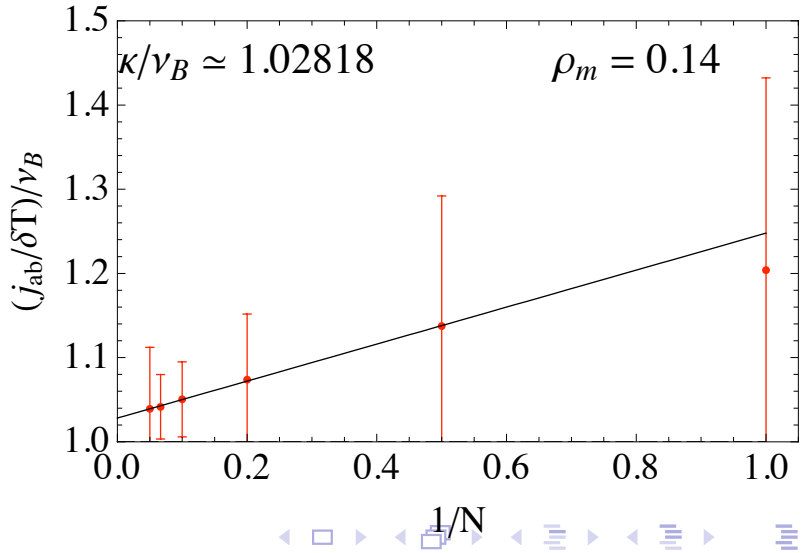
Numerical Results – Lattice Billiard

Thermal conductivity vs. ρ_m





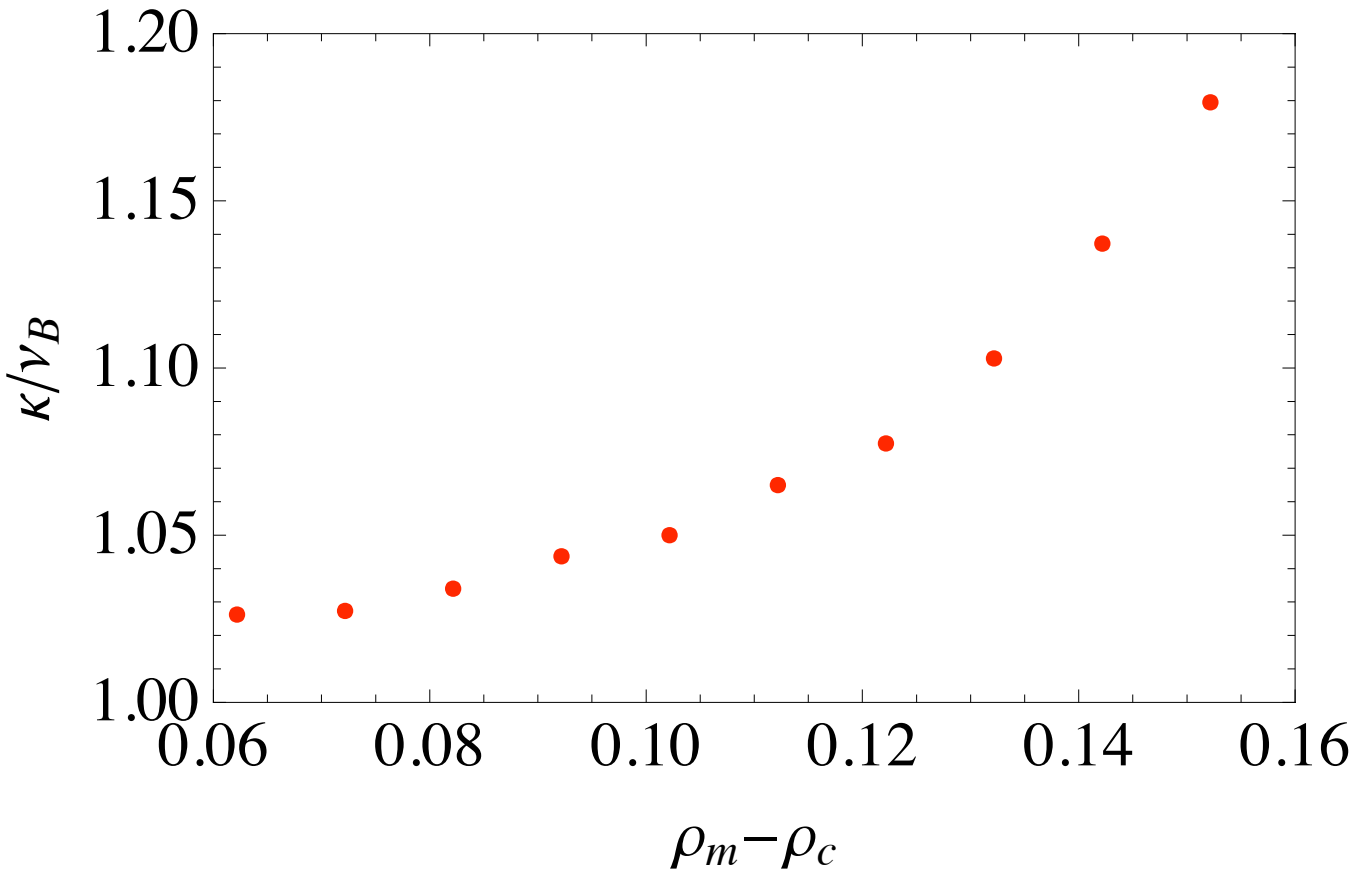




$(\rho = 0.36)$

Numerical Results – Lattice billiard

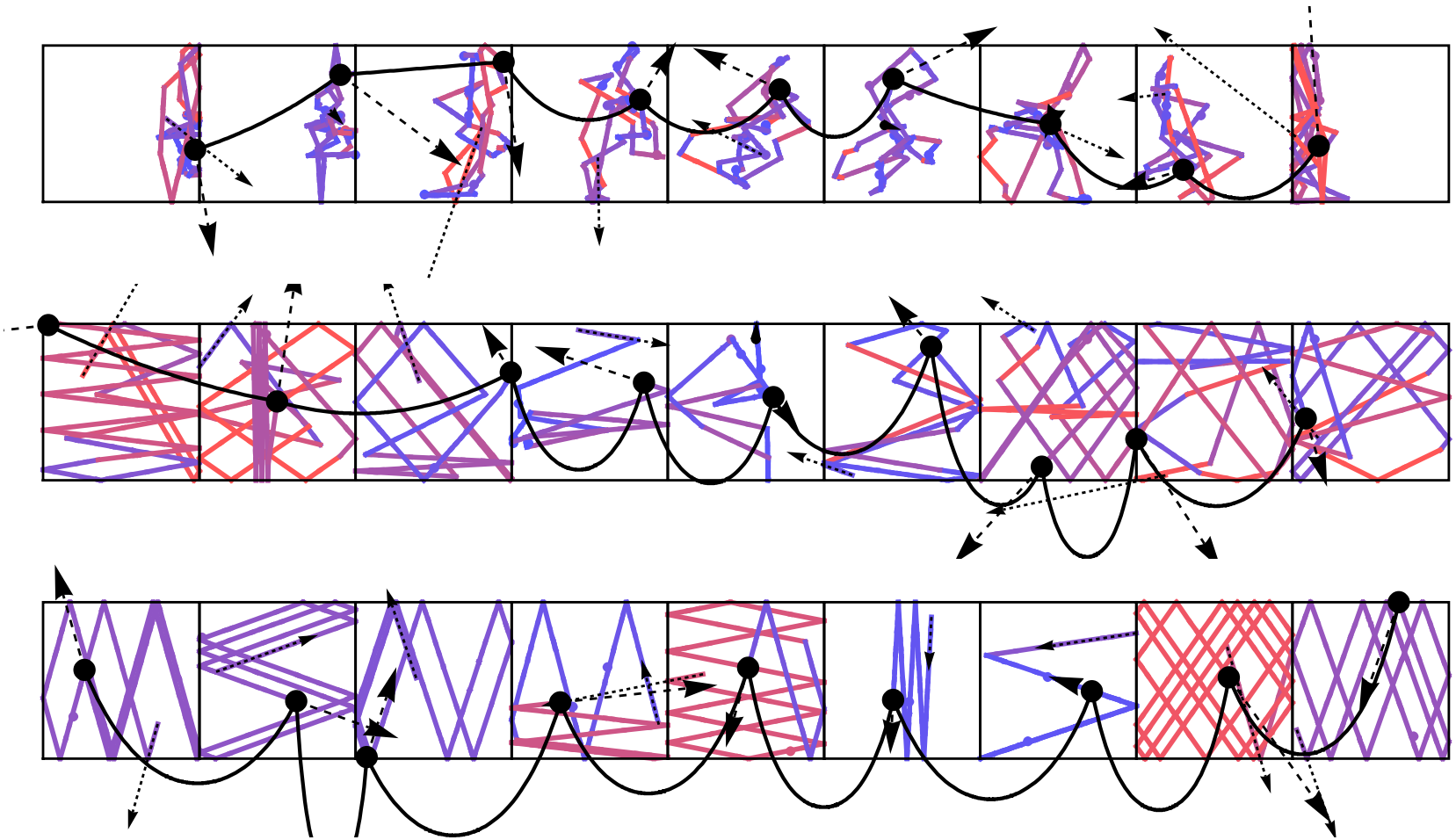
Thermal conductivity vs. ρ_{m}



$(\rho = 0.36)$

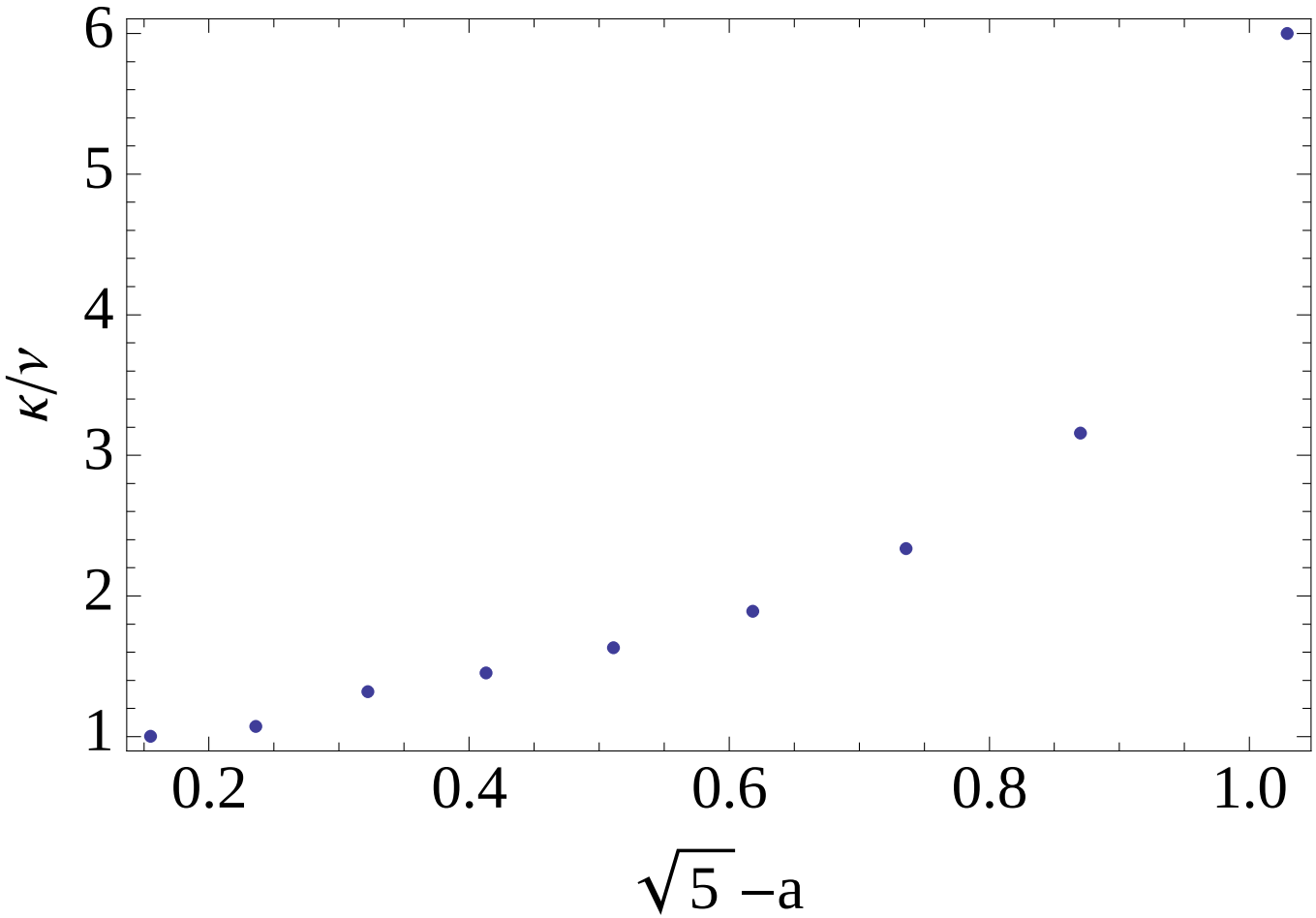
Square-Strings: Hard-Core Interaction at a Distance

TG and R Lefevere Phys Rev Lett **101** 200601 (2008)



Numerical Results – Square-strings

Thermal conductivity vs. *a*



Conclusions

1. Our mechanism of heat conduction proceeds in two stages : a fast local mixing stage which precedes energy exchanges leading to local thermalisation
2. The local equilibrium mechanism provides a simple accurate stochastic description of lattice billiards
3. The thermal conductivity vanishes at the critical geometry
4. The transport properties of the stochastic system can be computed assuming local thermal equilibria and reduce to a dimensional form
5. A similar two-stage mechanism is encountered in aerogels