

Heat Conductivity from Molecular Chaos Hypothesis in Locally Confined Billiard Systems

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We study the transport properties of a large class of locally confined Hamiltonian systems, in which neighboring particles interact through hard-core elastic collisions. When these collisions become rare and the systems large, we derive a Boltzmann-like equation for the evolution of the probability densities. We solve this equation in the linear regime and compute the heat conductivity from a Green-Kubo formula. The validity of our approach is demonstrated by comparing our predictions with the results of numerical simulations performed on a new class of high-dimensional defocusing chaotic billiards.

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The understanding of Fourier's law and the computation of the heat conductivity in Hamiltonian systems as a function of temperature and of the physical parameters remains to this day a challenging issue [1]. In particular, establishing the necessary conditions the dynamics must satisfy so as to justify a first principles based derivation of Fourier's law has been the subject of ongoing discussions.

As a generic model of heat transfer in insulating crystalline solids, one often considers a lattice of coupled particles with nearest-neighbor interactions whose motion obeys Hamilton's equations. Thus consider N particles of unit masses located on a one-dimensional lattice with positions and momenta $(\mathbf{q}, \mathbf{p}) \equiv \{(\mathbf{q}_i, \mathbf{p}_i)\}_{1 \leq i \leq N}$, with $\mathbf{q}_i, \mathbf{p}_i \in \mathbb{R}^d$. The Hamiltonian H takes the form

$$H(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^N \left[\frac{p_i^2}{2} + V(\mathbf{q}_i) + U(\mathbf{q}_i - \mathbf{q}_{i+1}) \right], \quad (1)$$

where V represents the interaction with the external substrate and U the nearest-neighbor interactions.

After Peierls' work [2], all attempts to give a satisfactory derivation of Fourier's law in mechanical systems have focused on the study of weakly anharmonic dynamics. Using the Peierls-Boltzmann equation, recent works have studied the effects of phonon collisions on the heat conductivity [3–7]. In this context, the conductivity may be interpreted as a collision frequency between phonons.

In this Letter, we focus on the opposite limit, namely, extremely anharmonic interactions, and, under minimal assumptions on the chaotic nature of the dynamics, identify a class of models which display a universal response to nonequilibrium thermal constraints. The motivation for this study is twofold: first, the heat conductivity can be computed from first principles and takes a simple form; second, as pointed out in [8], such systems of locally confined particles in interaction find concrete applications in the study of aerogels, materials in which gas particles are trapped in nanosize pores and rarely interact among them-

selves. Assuming the validity of a Boltzmann-like equation to describe such systems of rarely interacting particles when they become large, we show that the heat conductivity of such systems is generically equal to the average frequency of interaction between the systems' components, i.e., irrespective of the detailed geometric properties of the confinement mechanism. This will be checked in detail by numerical simulations, showing the universality and power of the Boltzmann approach to analyze the transfer of heat in the mechanical systems we study.

To be specific, we consider the case of interaction potentials which take only the values zero inside a region $\Omega_U \subset \mathbb{R}^d$ with smooth boundary Λ of dimension $d - 1$, and infinity outside. Likewise, the pinning potential V is assumed to be zero inside a bounded region Ω_V and infinity outside, implying that the motion of a single particle remains confined for all times. The regions Ω_U and Ω_V being specified, the dynamics is equivalent to a billiard in higher dimension. An important quantity in such models is the average rate of collisions between nearest-neighbors under equilibrium conditions. We will be specifically concerned with the limit of rare collision events.

The shape of the region Ω_V determines the nature of the local dynamics. In Ref. [8], Ω_V was chosen to be a semi-dispersive billiard with bounded horizon, thus ensuring strong chaotic properties of the dynamics. In particular the fast decay of correlations of the local dynamics was invoked to set up a stochastic equation describing the energy exchange dynamics. It is our purpose to show that this assumption can be relaxed: local ergodicity is enough to warrant the identity between heat conductivity and frequency of energy exchanges. We regard this as an important result which further validates the analogy between this class of models and aerogels whose nanopores need not have dispersing properties.

Examples of the simplest type of billiards we may consider are periodic arrays of square boxes in two dimensions in each of which a single hard disk particle moves freely,

but can still perform collisions with neighboring disks by interacting through the confining walls, for instance, provided we let the cells overlap a bit. The specific nature of the interaction mechanism at play is, however, not relevant in our formalism. We will instead consider point particles moving freely in two-dimensional square boxes of unit sides and interacting among nearest neighbors when the Euclidean distance between them becomes equal to a parameter which we denote by a . At that point, they exchange their longitudinal velocities, i.e., the velocity components in the direction of their relative motion. We refer to this model as the square-strings model. The interaction may be depicted by attaching strings of lengths a separating neighboring particles, as shown in Fig. 1. In this case, we take $\Omega_V = [-1/2, 1/2]^2$, and $\Omega_U = \mathbb{D}_{(-1,0)}^2(a)$, the disk of radius a with center at $(-1, 0)$. We note that, in the absence of interactions, the dynamics of the individual particles is pseudointegrable; it is ergodic on the configuration space for most values of the velocity directions, but is known to be nonmixing. We will consider this model in some details below and provide numerical evidence that the analysis which follows applies to it.

This model can be compared with a simpler class of complete exchange models, specified by square well potentials, obtained from Eq. (1) with $d = 1$, as a limit of models with smooth interaction potentials. In this case, $\Omega_V = [-b, b]$ and $\Omega_U = [-a, a]$. Each particle on the lattice moves freely on a one-dimensional cell of size $2b$, changing directions at the boundaries. The interaction between a pair of particles acts when the difference between the positions of the two particles reaches the value a , at which point they exchange their velocities.

In the general d -dimensional setup, the particles move freely inside their respective cells, bouncing off the walls elastically, until the vector $\mathbf{q}_i - \mathbf{q}_{i+1}$ (respectively $\mathbf{q}_{i-1} - \mathbf{q}_i$) reaches the boundary Λ . The corresponding particles then exchange the components of their velocities in the direction normal to the boundary Λ , i.e., longitudinal to the direction of their relative motion.

The Hamiltonian (1) may be written as a sum of local terms, $h_i(\mathbf{p}, \mathbf{q}) = p_i^2/2 + V(\mathbf{q}_i) + 1/2[U(\mathbf{q}_{i-1} - \mathbf{q}_i) + U(\mathbf{q}_i - \mathbf{q}_{i+1})]$. This allows one to define a function de-

scribing the local transfer of energy by computing the variation in time of the local energy h_i along the solutions of the equations of motion, $\frac{d}{dt}h_i(\mathbf{p}, \mathbf{q}) = j_{i-1} - j_i$, where the local energy current between sites i and $i + 1$ is defined as $j_i \equiv \frac{1}{2}(\mathbf{p}_i + \mathbf{p}_{i+1}) \cdot \nabla U(\mathbf{q}_i - \mathbf{q}_{i+1})$, which, for hard-core interactions, becomes

$$j_i = -\frac{1}{2}\delta_\Lambda(\mathbf{q}_i - \mathbf{q}_{i+1})|p_{i+1}^\perp - p_i^\perp|^+ [(p_{i+1}^\perp)^2 - (p_i^\perp)^2], \quad (2)$$

where $|x|^+ = x$, if $x \geq 0$, and 0 otherwise, $p_i^\perp = \mathbf{p}_i \cdot \hat{\mathbf{n}}$ is the component of the vector \mathbf{p}_i in the direction of the unit vector $\hat{\mathbf{n}}$, normal to the boundary Λ , and δ_Λ denotes the delta function concentrated on this boundary. The first factor corresponds to the localization of the collisions in configuration space, the second one gives the rate at which collisions occur and the last one corresponds to the exchange of longitudinal components of the kinetic energies.

Starting from the Liouville equation for the evolution of probability densities on phase space, it is straightforward to derive an equation for the evolution of the probability density of a single particle in a given cell. It involves the probability distribution of the pairs of particles which consist of the particle itself and either of its nearest-neighbors on the lattice. The Boltzmann approximation simply amounts to assuming that this two-particle distribution factorizes in terms of the one-particle distributions f_i at each site. To justify this assumption, one needs to show that a version of molecular chaos holds in our models. Namely, that the dynamical variables involved in the successive collisions between two neighbors are independent at the times of collisions. For that purpose, we require two ingredients: first, local correlations are typically destroyed after a collision between neighboring particles; second, the number of particles must be very large, so that in the long run, the whole system plays the role of a reservoir for the specified pair of nearest neighbors. How these conditions are realized in the models we consider and, in particular, in the square-strings model which we test numerically, is not yet fully elucidated. We interpret the first condition as requiring interactions to be rare compared to the collisions within a single cell. In the

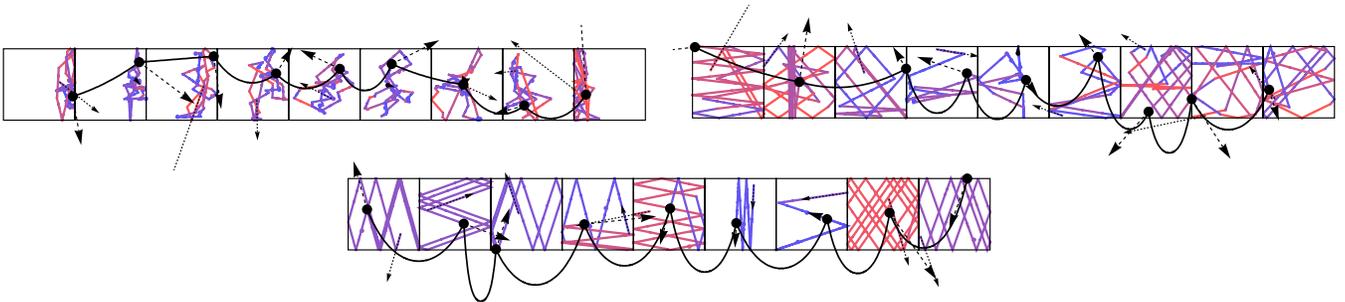


FIG. 1 (color online). Typical trajectories of the square-strings model, displayed for increasing values of a , color coded (shaded) from blue (dark gray) to red (gray) according to their energies. Small and large arrows indicate initial and final velocities, respectively. For large a , the system appears to be near-integrable, reflecting the rarity of interactions, but is nevertheless fully chaotic.

square-strings model, it amounts to taking the maximal separation close to the length of the diagonal joining opposite corners of neighboring boxes ($\equiv\sqrt{5}$), as in the third panel of Fig. 1.

We denote by $\underline{f} = \{f_i(\mathbf{p}, \mathbf{q}, t)\}_{1 \leq i \leq N}$, the set of the marginal probability distributions of each particle in each cell. The Boltzmann equation for this set of probability densities is

$$\frac{d}{dt} f_i(\mathbf{p}, \mathbf{q}, t) = -\mathbf{p} \cdot \nabla_{\mathbf{q}} f_i + L^w f_i + L_{i,i+1}^c(\underline{f}) + L_{i,i-1}^c(\underline{f}). \quad (3)$$

Here L^w accounts for the collisions of the particles with the walls of their respective cells, and $L_{i,i\pm 1}^c$ for the collisions of the i th particle with the $(i \pm 1)$ th, viz.

$$L_{i,i\pm 1}^c(\underline{f}) = \int d\mathbf{p}_a d\mathbf{q}' \delta_{\Lambda}(\mathbf{q} - \mathbf{q}') |p^{\perp} - p_a^{\perp}|^+ \times [f_{i\pm 1}(\mathbf{p}_b, \mathbf{q}') f_i(\mathbf{p}_c, \mathbf{q}) - f_i(\mathbf{p}, \mathbf{q}) f_{i\pm 1}(\mathbf{p}_a, \mathbf{q}')], \quad (4)$$

with $p_b^{\perp} = p^{\perp}$, $p_c^{\perp} = p_a^{\perp}$, $\mathbf{p}_c - p_c^{\perp} \hat{\mathbf{n}} = \mathbf{p} - p^{\perp} \hat{\mathbf{n}}$, and $\mathbf{p}_b - p_b^{\perp} \hat{\mathbf{n}} = \mathbf{p}_a - p_a^{\perp} \hat{\mathbf{n}}$. One can check that the distribution

$$\mu_{\text{eq}} \equiv \prod_{i=1}^N f_i(\mathbf{p}_i, \mathbf{q}_i) = Z^{-1} \prod_{i=1}^N e^{-\beta p_i^2/2} \mathbf{1}_{\Omega_v}(\mathbf{q}_i) \quad (5)$$

is stationary for any inverse temperature β . Applied to this distribution, the advection term in Eq. (3) is zero except on the cell borders where it cancels with $L^w f_i$. β may be fixed by imposing identical thermal boundary conditions at both ends of the lattice.

When the system is set out of equilibrium by imposing different temperatures at its boundaries, we proceed with a standard Chapman-Enskog expansion around a local equilibrium distribution,

$$\mu_{\text{leq}} \equiv \prod_{k=1}^N f_k(\mathbf{p}_k, \mathbf{q}_k) = Z^{-1} \prod_{k=1}^N e^{-\beta_k p_k^2/2} \mathbf{1}_{\Omega_v}(\mathbf{q}_k), \quad (6)$$

with $\beta_k = \hat{\beta}(k/N)$ for some smooth function $\hat{\beta}$, taking as a small parameter the local temperature gradient. Plugging Eq. (6) into (3), we observe that only terms of second-order in the temperature gradient survive. This is in contrast with the case of an ordinary gas of colliding particles. This simplification occurs because the advection term of the Boltzmann equation (3) acts only on the position variable within each cell and therefore not as a gradient on the lattice dependent variables. This means that local averages with respect to the distribution (6) are identical to local averages with respect to the true nonequilibrium stationary state, denoted $\langle \cdot \rangle_{\text{neq}}$, up to $\mathcal{O}(1/N^2)$ corrections.

In particular, one may compute the average current (2) with respect to the measure (6) and get (with $\beta_i = T_i^{-1}$),

$$\langle j_i \rangle_{\text{neq}} = -\nu(T_i)(T_{i+1} - T_i) + \mathcal{O}(1/N^2), \quad (7)$$

where, $\nu(T_i) = \langle \delta_{\Lambda}(q_i - q_{i+1}) |p_i^{\perp} - p_{i+1}^{\perp}|^+ \rangle_{T_i}$ is readily interpreted as the average collision frequency between the neighbors i and $i + 1$, with respect to a global equilibrium measure at temperature T_i , Eq. (5). This computation therefore shows that the conductivity $\kappa(T_i)$, defined as

$$\kappa(T_i) \equiv \lim_{N \rightarrow \infty} -\frac{\langle j_i \rangle_{\text{neq}}}{T_{i+1} - T_i}, \quad (8)$$

is identical to $\nu(T_i)$. Furthermore a simple scaling argument shows that $\kappa(T_i) = \nu(T_i) = \sqrt{T_i} \nu$, where ν denotes the collision frequency computed at unit temperature. Being the result of an equilibrium integration, the frequency may be computed with arbitrary precision.

To get a better picture of the process that is described by the Boltzmann equation (3), we linearize the equation around the global equilibrium solution (5). Doing so, we obtain an equation similar to (3), but with the collision operators $L_{i,i\pm 1}^c$ now replaced by L_i^{lin} ,

$$\frac{d}{dt} f_i(\mathbf{p}, \mathbf{q}, t) = -\mathbf{p} \cdot \nabla_{\mathbf{q}} f_i + L^w f_i + 2L_i^{\text{lin}} f_i, \quad (9)$$

where the linearized collision operator L_i^{lin} is obtained from Eq. (4) by replacing $f_{i\pm 1}$ by equilibrium distributions at common inverse temperature β .

The interpretation of the stochastic process described by the linearized collision operator is straightforward: when collisions take place, the particles velocities are updated as though they collided with stochastic thermal walls at inverse temperature β [9]. At each collision, the new velocities are independent from the previous ones.

With this prescription, we now compute the conductivity using the Green-Kubo formula, which is derived as follows. Integrated over time, the energy current between sites i and $i + 1$ takes the form

$$J_i([0, t]) = \int_0^t j_i(s) ds = \frac{1}{2} \sum_{0 \leq s_i^k \leq t} [p_i^{\perp}(s_i^k)^2 - p_{i+1}^{\perp}(s_i^k)^2], \quad (10)$$

where the $(s_i^k)_{k \in \mathbb{N}}$ are the successive collision times between particles i and $i + 1$. The Green-Kubo formula reads in our case,

$$\kappa_{\text{GK}}(T) = \frac{1}{2NT^2} \lim_{t \rightarrow \infty} \frac{1}{t} \sum_{i,k=1}^N \langle J_i([0, t]) J_k([0, t]) \rangle_T. \quad (11)$$

Using the expression (2) and (10), translation-invariance, and the independence of the transfer of energy at each collision, we get, after some calculations,

$$\kappa_{\text{GK}}(T) = \frac{1}{8T^2} \langle \delta_{\Lambda}(\mathbf{q}_0 - \mathbf{q}_1) |p_0^{\perp} - p_1^{\perp}|^+ [(p_0^{\perp})^2 - (p_1^{\perp})^2] \rangle_T, \quad (12)$$

which, after further computations turns out to be equal to the collision frequency, $\kappa_{\text{GK}}(T) = \nu(T)$.

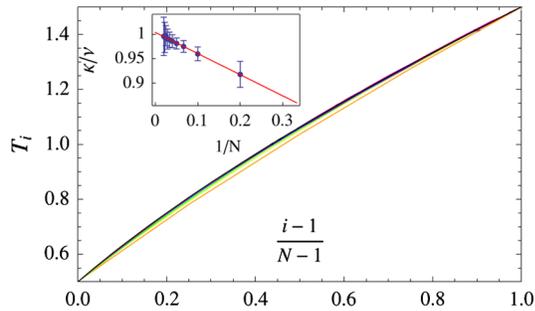


FIG. 2 (color online). Nonequilibrium temperature profiles of the square-strings model with $a = 2.08$, for increasing values of $N = 5, 10, \dots, 50$. The black curve is the stationary solution of the heat equation. The inset displays the corresponding measurements of $\langle \kappa(T_i)/\nu(T_i) \rangle$. The infinite N extrapolation, $\kappa/\nu = 1.0037$, is the approximate heat conductivity reported in Table I.

The square-strings model displayed in Fig. 1 lends itself to a detailed study of the dependence of the ratio κ/ν on the parameter values a .

To this end we consider systems of varying sizes N with both ends in contact with stochastic thermal baths at respective temperatures $T_- = \frac{1}{2}$ and $T_+ = \frac{3}{2}$. This gives rise to nonequilibrium stationary states with temperature profiles such as displayed in Fig. 2, which, as N increases, approach the corresponding solution of the heat equation, $\partial_x[\kappa(T(x))\partial_x T(x)] = 0$, with $\kappa(T(x)) \propto \sqrt{T(x)}$. The ratio κ/ν is obtained by linearly extrapolating to $N \rightarrow \infty$ finite N measurements of the spatial averages of $\kappa(T_i)/\nu(T_i)$, with $\kappa(T_i)$ defined by Eq. (8) and $\nu(T_i)$ the collision frequency at the local temperature, as functions of $1/N$.

These values are reported in Table I. Notice the excellent agreement with the prediction $\kappa = \nu$, Eq. (12), as the value of the parameter a gets closer to its maximal allowed value, the limit of rare collisions, in close agreement with the results presented in [8] for a class of coupled semidispersing billiards. In particular, we underline that the parameter range of validity of our result is very similar to that observed in [8], which further validates that it is independent of the detailed nature of the local dynamics.

To summarize, we have showed that the derivation of Fourier's law in a large class of locally confined particle systems with hard-core interactions can be achieved from a Boltzmann-type approach with the main result that, in the appropriate limits, the heat conductivity is identified with the collision frequency.

The same identity was derived in [8] in the context of semidispersing billiards. The comparison is interesting since, in contrast, chaos in the square-strings model results from a defocusing mechanism which takes place after particles interact. The identity between conductivity and collision frequency therefore proves to be more general as

TABLE I. Measurements of κ/ν for selected values of a , obtained from data similar to Fig. 2. Our results indicate that $\kappa/\nu \rightarrow 1$ as $a \rightarrow \sqrt{5}$, in agreement with Eq. (12).

| $\sqrt{5} - a$ | κ/ν | $\sqrt{5} - a$ | κ/ν | $\sqrt{5} - a$ | κ/ν |
|----------------|--------------|----------------|--------------|----------------|--------------|
| 1.029 | 6.000 | 0.618 | 1.892 | 0.322 | 1.320 |
| 0.870 | 3.159 | 0.511 | 1.632 | 0.236 | 1.0718 |
| 0.736 | 2.336 | 0.413 | 1.452 | 0.155 | 1.0037 |

it accounts for the transport properties of systems lacking the local mixing property. In fact, the only dynamical property which is *a priori* necessary in our derivation is ergodicity of the local dynamics, i.e., in the absence of interactions. This property guarantees that two neighbors always interact provided the coupling is switched on, and that the fraction of time during which they interact is proportional to a fixed geometrical factor which can be adjusted by tuning the systems' parameters.

The square-strings model is a perfect example of a system which lends itself with ease to a precise and reliable numerical analysis, while retaining the molecular chaos property. The square-strings model is actually a kind of higher dimensional fully chaotic stadium and displays a very rich structure of dynamical properties.

We regard the proof of the molecular chaos hypothesis upon which our computation relies as a promising and realistic way to eventually obtain a clear picture of the different mechanisms responsible for the origin of Fourier's law in a large class of mechanical systems.

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