

## Heat Conduction and Fourier's Law by Consecutive Local Mixing and Thermalization

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We present a first-principles study of heat conduction in a class of models which exhibit a new multistep local thermalization mechanism which gives rise to Fourier's law. Local thermalization in our models occurs as the result of binary collisions among locally confined gas particles. We explore the conditions under which relaxation to local equilibrium, which involves no energy exchange, takes place on time scales shorter than that of the binary collisions which induce local thermalization. The role of this mechanism in multiphase material systems such as aerogels is discussed.

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The transport property of thermal conductivity has been introduced as a phenomenological law by Joseph Fourier in 1822 [1]. Its molecular origins were later discovered with Boltzmann's and Maxwell's works on the kinetic theory of gases [2,3]. In metallic solids, the thermal conduction is mainly determined by the transport of electrons and thus related to the electric conductivity according to the Wiedemann-Franz law, as explained by Drude in 1900 [4]. In contrast, the thermal conductivity of nonmetallic solids results from the mutual scattering of sound waves due to the anharmonicities of the interatomic forces, as shown by Peierls in 1929 [5,6]. In all these systems, the microscopic mechanism of thermal conduction is the scattering of the energy carriers, which induces local thermalization in a single-stage process, and subsequent uniformization of temperature [7]. Yet, this one-stage scenario does not exhaust the possible microscopic mechanisms. Here, we prove that, in a further class of systems, local mixing can precede the start of energy transfer leading to local thermalization. On the basis of this mechanism, we provide a derivation of Fourier's law.

This new mechanism of local thermalization allows us to understand how materials can become excellent thermal insulators, as is the case with aerogels [8]. In these materials, a gas is trapped in a solid-state nanoporous matrix. The gas molecules collide with the walls of the nanopores more frequently than among themselves. Since the collisional transfer of energy is smaller with a stiff wall than with another free molecule, the changes of velocity orientation occur before a significant energy transfer. Accordingly, we envisage the mechanism where the wall collision frequency is shorter than the binary collision frequency.

In this respect, thermal conduction should proceed over three well-separated time scales,  $\tau_{\text{wall}} \ll \tau_{\text{binary}} \ll \tau_{\text{macro}}$ , which are: (i) the short time scale  $\tau_{\text{wall}}$  of the collisions on the solid walls, inducing the mixing of the particle positions and velocity orientations with negligible transfer of particle kinetic energy and no mass transport; (ii) the intermediate time scale  $\tau_{\text{binary}}$  of the binary collisions between pairs of particles, achieving a local thermodynamic

equilibrium at some locally defined temperature; and (iii) the long time scale  $\tau_{\text{macro}}$  of the macroscopic relaxation of the Fourier modes.

To demonstrate this mechanism, we consider in this Letter Hamiltonian dynamical systems in which hard ball particles undergo elastic collisions either with immobile obstacles composing the solid matrix, or with each other. The obstacles form a lattice structure of cells, each confining a single mobile particle and preventing any mass transport. The motion of the particles is controlled by the geometry of the cells in such a way that the binary collisions only occur between nearest-neighboring mobile particles at a rate which can be switched off by shrinking the domain of motion within each cell. At the critical geometry where the binary collisions become impossible, the thermal conductivity vanishes with the binary collision frequency, in a way which can be rigorously calculated, as we show below. The remarkable result is that Fourier's law of heat transport can be established for this class of systems, based on the strong ergodic properties that they enjoy [9].

Under the assumption that binary collisions are seldom compared to wall collisions, the chaotic motion of individual particles within their cells induces a rapid decay of

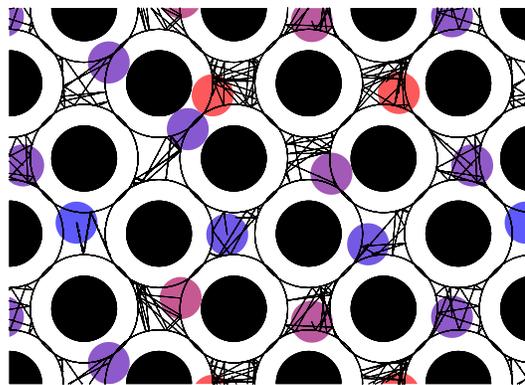


FIG. 1 (color online). Example of lattice billiard with rhombic tiling. The mobile disks are color coded from blue to red with growing kinetic energies. See text for details.

statistical correlations. As a consequence, the global multi-particle probability distribution of the system typically reaches local equilibrium distributions at the kinetic energy of each individual particle before energy exchanges proceed. This allows us to obtain a kinetic equation for the probability distribution of the local energies [10], which, under a Boltzmann-type assumption, reduces to a Boltzmann-Kac equation [11]. In contrast to the Boltzmann equation, which requires a further approximation, our kinetic equation can be fully justified thanks to the mixing property of the dynamics and the separation of the time scales  $\tau_{\text{wall}} \ll \tau_{\text{binary}}$ .

To be specific, we consider a system such as depicted in Fig. 1. It consists of a periodic two-dimensional array of discs of radii  $\rho_f$ . In every cell between those discs, we place a single mobile disc of radius  $\rho_m$ , large enough that the particles are confined to the regions between the discs. The shape of this region, which is a bounded dispersing billiard [12], only depends on the sum of the two radii  $\rho = \rho_f + \rho_m$ , which is kept constant.

Energy exchanges occur when two moving particles located in neighboring cells collide. Such binary collisions can take place provided the radii  $\rho_m$  of the moving particles is large enough. For a lattice with cells of sides  $l$ , binary collisions are thus possible above the critical value

$$\rho_c \equiv \sqrt{\rho^2 - (l/2)^2} < \rho_m < \rho. \quad (1)$$

In this regime, the system is a thermal conductor. On the contrary, it becomes a thermal insulator for  $\rho_m \leq \rho_c$ . The thermal conductivity vanishes as  $\rho_m \xrightarrow{\geq} \rho_c$  in an exactly calculable way.

In order to establish this result, we start from first principles. The system is of Hamiltonian character and the time evolution of the global probability distribution of the positions and velocities of all the  $N$  particles is described by the pseudo-Liouville equation [13]:

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

where  $-\mathbf{v}_a \cdot \partial_{\mathbf{r}_a}$  is the advection term expressing the changes of the probability distribution due to the free motion at the velocity  $\mathbf{v}_a$  of particle  $a$  inside its cell, the wall term  $K^{(a,k)}$  is the operator ruling the collisions of particle  $a$  on the fixed disc  $k$  in the corresponding cell, and  $B^{(a,b)}$  rules the binary collisions between the particles  $a$  and  $b$ . Without these last terms, the pseudo-Liouville equation would describe the relaxation of the probability distribution to the product of local distributions  $\prod_{a=1}^N \delta(\epsilon_a - mv_a^2/2)$  for all the particles at their respective kinetic energies  $\epsilon_a$ . This relaxation is driven by the local mixing of the single-cell dispersing billiards, which takes place over the short time scale  $\tau_{\text{wall}}$ . The important point is that the probability distribution has not yet reached a local Maxwellian distribution. The local thermalization is the outcome of the binary collisions which take place on the intermediate time scale  $\tau_{\text{binary}}$ . This stage of the process of heat conduction is in general utterly difficult to master in a mathematically controllable way. However, the fact that local mixing precedes local thermalization allows us to obtain a kinetic equation for the probability distribution of the energies of the particles:

$$P_N^{(\text{leq})}(\epsilon_1, \dots, \epsilon_N, t) \equiv \int \prod_{a=1}^N d\mathbf{r}_a d\mathbf{v}_a p_N(\mathbf{r}_1, \mathbf{v}_1, \dots, \mathbf{r}_N, \mathbf{v}_N, t) \prod_{a=1}^N \delta(\epsilon_a - mv_a^2/2), \quad (3)$$

where  $v_a \equiv \|\mathbf{v}_a\|$ . Integrating the pseudo-Liouville Eq. (2) with the local equilibrium distributions, the advective terms as well as the terms of the wall collisions vanish. We remain with the terms due to the binary collisions, which yield the following master equation [10]:

$$\begin{aligned} \partial_t P_N^{(\text{leq})}(\epsilon_1, \dots, \epsilon_N, t) = & \frac{1}{2} \sum_{a,b=1}^N \int d\eta [W_{(\epsilon_a + \eta, \epsilon_b - \eta) \rightarrow (\epsilon_a, \epsilon_b)} P_N^{(\text{leq})}(\dots, \epsilon_a + \eta, \epsilon_b - \eta, \dots, t) \\ & - W_{(\epsilon_a, \epsilon_b) \rightarrow (\epsilon_a - \eta, \epsilon_b + \eta)} P_N^{(\text{leq})}(\dots, \epsilon_a, \epsilon_b, \dots, t)], \end{aligned} \quad (4)$$

where

$$\begin{aligned} W_{(\epsilon_a, \epsilon_b) \rightarrow (\epsilon_a - \eta, \epsilon_b + \eta)} = & \frac{2\rho_m m^2}{(2\pi)^2 |\mathcal{L}_{\rho, \rho_m}(2)|} \int d\phi d\mathbf{R} \int_{\hat{\mathbf{e}}_{ab} \cdot \mathbf{v}_{ab} > 0} d\mathbf{v}_a d\mathbf{v}_b \hat{\mathbf{e}}_{ab} \cdot \mathbf{v}_{ab} \delta\left(\epsilon_a - \frac{m}{2} v_a^2\right) \delta\left(\epsilon_b - \frac{m}{2} v_b^2\right) \\ & \times \delta\left(\eta - \frac{m}{2} [(\hat{\mathbf{e}}_{ab} \cdot \mathbf{v}_a)^2 - (\hat{\mathbf{e}}_{ab} \cdot \mathbf{v}_b)^2]\right), \end{aligned} \quad (5)$$

is the transition rate of the binary collisions of energy transfer  $\eta$  between the neighboring particles  $a$  and  $b$ . In this expression,  $|\mathcal{L}_{\rho, \rho_m}(2)|$  is the volume of the billiard corresponding to two neighboring cells  $a$  and  $b$ , which can be approximated by the square of the volume of a single cell  $|\mathcal{B}_\rho|^2$ ,  $\phi$  is the angle of the unit vector  $\hat{\mathbf{e}}_{ab} = (\cos\phi, \sin\phi)$  connecting  $a$  and  $b$ , and  $\mathbf{R} = (\mathbf{r}_a + \mathbf{r}_b)/2$  the center of mass of the particles  $a$  and  $b$ . The transition rate  $W$  can be further expressed in terms of Jacobian elliptic functions [14]. The master equation (4) describes the time evolution as a

continuous-time stochastic process of Poisson type with exponential probability distributions for the waiting times between the random events of energy transfers due to the binary collisions. Accordingly, the master equation (4) shows that local thermalization is reached over the intermediate time scale  $\tau_{\text{binary}} \simeq 1/\nu_b$  of the binary collisions, which, in terms of the binary collision frequency, is given by

$$\begin{aligned} \nu_b &= \beta^2 \int d\epsilon_a d\epsilon_b d\eta W_{(\epsilon_a, \epsilon_b) \rightarrow (\epsilon_a - \eta, \epsilon_b + \eta)} e^{-\beta(\epsilon_a + \epsilon_b)}, \\ &= \sqrt{\frac{k_B T}{\pi m}} \frac{2\rho_m}{|\mathcal{B}_\rho|^2} \left( \int d\phi d\mathbf{R} \right), \end{aligned} \quad (6)$$

where  $\beta = 1/(k_B T)$  is the inverse of the temperature  $T$  multiplied by Boltzmann's constant  $k_B$ .

Starting from the master equation (4), we derive the heat equation

$$\partial_t T = \partial_x (\kappa \partial_x T), \quad (7)$$

for the local temperature  $T = T_a$  defined in terms of the kinetic energy of particle  $a$  averaged over the probability distribution (3),  $\langle \epsilon_a \rangle \equiv k_B T_a$ . The derivation of Eq. (7) from stochastic models such as defined by the master equation (4) requires the computation of correlation functions [15]. In particular the heat current between two neighboring cells involves an average with respect to the joint probability distribution of their energies and thus depends on their correlations. Assuming nonequilibrium boundary conditions, a systematic computation of the stationary state can be performed through a cluster expansion. Single-cell distributions, which solve the Boltzmann-Kac equation [11], give the first order solutions of this expansion, while pair correlations appear at the second order, and so on. For the stochastic system described by Eq. (4), it turns out that pair correlations are of second degree in the local temperature gradients and can therefore be neglected in the computation of the transport coefficient, which involves only terms linear in this quantity. We can thus limit the cluster expansion to first order and find the expression of the coefficient of thermal conductivity:

$$\frac{\kappa}{l^2} = \sqrt{\frac{k_B T}{\pi m}} \frac{2\rho_m}{|\mathcal{B}_\rho|^2} \left( \int d\phi d\mathbf{R} \right). \quad (8)$$

We verified this result by direct numerical simulations of Eq. (4). Alternatively,  $\kappa$  can be defined through a Green-Kubo formula. The result (8) shows that  $\kappa$  is given by the  $\delta(t)$  part of the energy current-current correlation discussed in Ref. [15]. We notice that this result holds here even though the heat current does not have the gradient form of [15], i.e., it cannot be written as the difference of two local functions. The details will be presented elsewhere [16].

The comparison between Eqs. (6) and (8) shows the equality of the thermal conductivity and collision frequency of the stochastic process described by Eq. (4). By

extension, the same holds of the corresponding properties of the billiard system in the limit  $\rho_m \rightarrow \rho_c$ :  $\lim_{\rho_m \rightarrow \rho_c} \kappa / (l^2 \nu_b) = 1$ . Furthermore, the thermal conductivity can be explicitly calculated in this limit and shown to vanish as the third power of the difference  $\rho_m - \rho_c$ . Indeed, the geometric integral appearing in both Eqs. (6) and (8) vanishes as

$$\int d\phi d\mathbf{R} = c_3 (\rho_m - \rho_c)^3 + c_4 (\rho_m - \rho_c)^4 + \dots, \quad (9)$$

where the coefficients in this expansion can be computed according to the specific geometry of collision events [14].

Numerical computations of the quantities computed in Eqs. (6) and (8) are shown in Fig. 2, asserting the validity of the stochastic description (4) on the one hand and the computation of its properties on the other.

Finally, the local mixing property can be characterized by the Lyapunov exponents measuring the stretching and contraction of phase-space volumes. Remarkably, all these exponents can be analytically calculated in the same critical limit where the binary collision frequency vanishes. In this limit, the particle velocities share a Maxwellian probability distribution at the inverse temperature  $\beta$  while the particles become independent. Accordingly, a system containing  $N$  particles presents the  $N$  positive Lyapunov exponents

$$\lambda_i = \lambda_+ \sqrt{\frac{2}{m\beta} \ln \frac{N}{i - 1/2}}, \quad i = 1, \dots, N, \quad (10)$$

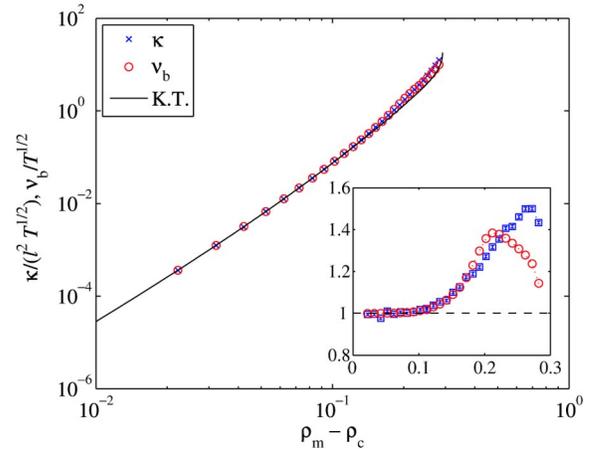


FIG. 2 (color online). Thermal conductivity  $\kappa$  in reduced units, computed by molecular dynamics from the heat exchange of a single particle with stochastically thermalized neighbors, and binary collision frequency  $\nu_b$ , as functions of  $\rho_m - \rho_c$ , compared to our theoretical calculations (6) and (8) (solid line). The inset shows the ratios between  $\nu_b$  and  $\kappa$  and the right-hand side of (6) and (8). The computations were performed with a rhombic cell in contact with stochastically thermalized cells on each sides, in which case  $c_3 = 128\rho_c/(3l^2)$  and  $c_4 = 256\rho_c^2/(3l^4)$  in Eq. (9). The sum of radii is here fixed to the value  $\rho = \rho_f + \rho_m = 9/25$ .

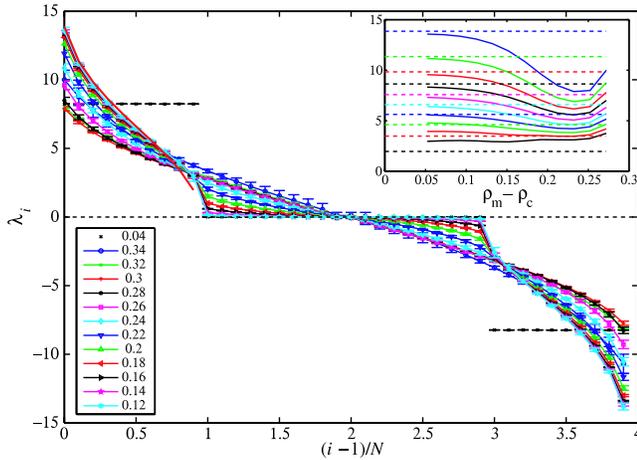


FIG. 3 (color online). Lyapunov exponents  $\lambda_i$  versus their index  $i$ . The numbers in the legend correspond to the values of  $\rho_m$ . The first one,  $\rho_m = 0.04 < \rho_c$ , yields the positive exponent  $\lambda_+$  associated to isolated cells, with all the particles at the same speed. The solid red line is the first half of the spectrum as predicted by Eq. (10). The inset shows  $\lambda_i$  versus  $\rho_m - \rho_c$  for the first half of the positive exponents,  $\lambda_1, \dots, \lambda_N$  and compares them to the asymptotic value (10) (dashed lines). The computations were performed with a rhombic channel of size  $N = 10$  cells,  $\rho = 9/25$ .

where  $\lambda_+$  is the positive Lyapunov exponent of a single isolated particle moving at unit speed.  $2N$  exponents are zero in the said limit and the  $N$  remaining exponents take the negative values  $-\lambda_i$ . The sum of all the exponents vanishes since the system is Hamiltonian and satisfies Liouville's theorem. The system is thus chaotic with an extensive Kolmogorov-Sinai entropy per unit time given by  $h_{KS} = N\lambda_+\sqrt{\pi/(2m\beta)}$ .

Figure 3 shows the agreement between the numerically computed Lyapunov exponents and Eq. (10), in the limit where the system becomes insulating.

To conclude, we have presented in this Letter a mechanism of heat conduction which proceeds in two stages and involves no mass transport. The first stage is a local mixing phase which takes place in the individual cells and involves no energy transfer between them. This stage thus induces the relaxation of phase-space distributions to local equilibrium without thermalization. The second stage is the energy transfer which leads to local thermalization and can be efficiently described in probabilistic terms by means of our master equation. The uniformization of the temperature over the whole system can then proceed as described by the heat equation. Whereas the first-principles derivation of Fourier's law is problematic based on the standard one-stage local thermalization mechanism, it is remarkable that it can be carried out in the presence of this additional local equilibrium mechanism. We notice that both mechanisms correspond to physically distinct limits for the heat conductivity. In the standard one-stage mechanism, the ballistic transport of the energy carriers is hampered by scat-

tering so that the theory should there demonstrate a finite conductivity with respect to an unperturbed situation where the conductivity is unbounded. In contrast, in the two-stage mechanism we here describe, the thermal conductivity vanishes in the reference system, allowing the first-principles derivation of Fourier's law. This two-stage mechanism is encountered in aerogels where the thermal conductivity takes the smallest known values. Our analysis therefore suggests that fundamental insight into the phenomenon of heat conductivity could be obtained by the experimental study of aerogels.

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