Energy transport in anharmonic lattices close and far from equilibrium

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The problem of stationary heat transport in the Fermi-Pasta-Ulam chain is numerically studied showing that the conductivity diverges in the thermodynamic limit. Simulations were performed with time-reversible thermostats, both for small and large temperature gradients. In the latter case, fluctuations of the heat current are shown to be in agreement with the recent conjectures of Gallavotti and Cohen [Phys. Rev. Lett. 74, 2694 (1995)].

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I. INTRODUCTION

The problem of heat conduction in one-dimensional insulating solids is very old. The celebrated Peierls’ theory [1] was successful in describing the low-temperature dependence of the thermal conduction coefficient, clarifying the basic role of Umklapp scattering induced by nonlinearity. However, for sufficiently high energies/temperatures, where the usual picture of weakly interacting phonons is no longer appropriate, one has to face a fully nonlinear problem and a complete analytical solution seems hardly feasible.

Accordingly, in such a regime, the problem has been attacked several times by means of nonequilibrium molecular-dynamics (see Ref. [2] and the bibliography therein). This amounts to solving numerically the microscopic (classical) equations of motion, with the principal goals of recovering the macroscopic heat-diffusion law and of measuring the corresponding transport coefficient. However, even this program turned out to be far from trivial, especially in one spatial dimension, where the interpretation of the numerical analysis appears to be rather controversial.

The only clear results refer to some 1D toy models, characterized by a non-smooth interaction, like the so-called ding-a-ling model [3] and its simplified version studied in Ref. [4]. The remarkable success of such artificial systems in producing a “normal” (i.e. length-independent) heat conductivity is claimed to follow from the strong inhibition of coherent soliton propagation (see, however, Ref. [5] for a counterexample). Accordingly, the main mechanism at work is the diffusive transport of the energy induced by the underlying chaotic dynamics, which thus ensures the validity of the Fourier law.

As soon as one turns to the more realistic case of smooth interaction potentials, the scenario is definitely more ambiguous. For instance, it is claimed that the conductivity of a diatomic Toda lattice is finite or diverging depending on the mass ratio [6]. For the Fermi-Pasta-Ulam (FPU) chain, the results reported in Ref. [2] and in this paper do not show any evidence of a normal conductivity. In every case, there is no clear explanation of...
the observed phenomenology, even in the limit of small applied gradients, so that it is worth reconsidering the whole problem.

This is not, however, our only motivation. Recently, the approach to non-equilibrium statistical mechanics through the introduction of time-reversible thermostats proved to be rather effective in several test problems \[7\]. In fact, if a system, besides being time-reversible, is “sufficiently chaotic”, the tools developed for strictly hyperbolic systems allow for some statistical predictions even far from equilibrium \[8\]. Relevant numerical tests have been performed on shear-flow \[9\] and electrical conduction models \[10\]. In the second part of the present work, we successfully test these ideas also for the heat conduction problem.

More specifically, in section II we introduce the model equations, while section III is devoted to a brief description of the microscopic quantities of interest. Macroscopic properties of heat conduction are discussed in section IV, and the predictions of the “chaotic hypothesis” are tested in section V. The open problems and future perspectives are shortly summarized in section V. Finally, the expression for the heat flux measured in the simulations is derived in the Appendix.

### II. MODELS WITH TIME-REVERSIBLE THERMOSTATS

We consider a chain of \(N\) anharmonic oscillators, denoting with \(q_i\) the displacement of the \(l\)-th particle from its equilibrium position. The lattice has fixed boundary conditions, \(q_0 = q_{N+1} = 0\). In the bulk (\(l = 2, \ldots, N - 1\)), the equations of motion are purely hamiltonian, namely

\[
\ddot{q}_l = f_l - f_{l+1} , \tag{1}
\]

where \(f_l = -V'(q_l - q_{l-1})\) is the force resulting from the interaction potential \(V\) (the prime denotes derivative with respect to the argument) acting between neighbouring particles. In the following we will consider the FPU potential

\[
V(x) = \frac{x^2}{2} + \beta \frac{x^4}{4} \tag{2}
\]

with \(\beta = 0.1\). We anticipate that the results described here in the following do not appear to be peculiar of this choice of the potential. A similar scenario has been found for different choices of \(V\).

The first and the \(N\)-th oscillators interact with two heat reservoirs operating at different temperatures, \(T_L\) and \(T_R\), respectively (without loss of generality, we assume that \(T_L > T_R\)), in order to induce a heat flux through the chain. Their equations of motion are

\[
\begin{align*}
\dot{q}_1 &= -\zeta_L \dot{q}_1 + f_1 - f_2 \\
\dot{q}_N &= -\zeta_R \dot{q}_N + f_N - f_{N+1} . \tag{3}
\end{align*}
\]

The action of the thermostats is microscopically modelled by the “thermal” variables \(\zeta_L, \zeta_R\), which evolve according to the Nosé-Hoover dynamical equations \[1\]

\[
\begin{align*}
\dot{\zeta}_L &= \frac{1}{\Theta^2} \left( \frac{\dot{q}_L^2}{T_L} - 1 \right) \\
\dot{\zeta}_R &= \frac{1}{\Theta^2} \left( \frac{\dot{q}_R^2}{T_R} - 1 \right) , \tag{4}
\end{align*}
\]

where the time \(\Theta\) is the thermostat response time. The above prescriptions imply that the kinetic energy of the boundary particles fluctuates around the imposed average value, thus simulating a “canonical” dynamics. In the limit case \(\Theta \to 0\), one has the so-called isokinetic (or Gaussian) thermostat: the kinetic energy is exactly conserved and the action of the thermal bath is properly described without the need to introduce a further dynamical variable, since \(\zeta\) becomes an explicit function of the \(\dot{q}_s\) \[1\]. We shall see that there is a price to pay for the simplification of the dynamical equations: a larger thermal resistance at the boundaries.

For all values of \(\Theta\), the equations of motion are left invariant under time-reversal composed with the involution \(I\) defined as \(\dot{q}_i \to -\dot{q}_i, \zeta \to -\zeta\) (notice that the \(\zeta_s\) are momentum-like quantities \[11\]). For a discussion of time reversibility in such thermostatted models and its implications to nonequilibrium statistical mechanics see Ref. \[12\].
III. MICROSCOPIC DEFINITION OF THE THERMODYNAMIC QUANTITIES

Let us define the local energy density of the chain as 
\[ h_l(x, t) = \sum_l h_l \delta(x - x_l), \]
where \( x_l = la + q_l \) is the position of the \( l \)-th particle in a lattice of spacing \( a \), while 
\[ h_l := \frac{p_l^2}{2} + \frac{1}{2} [V(q_{l+1} - q_l) + V(q_l - q_{l-1})] \tag{5} \]
is the energy per particle (as usual, all the masses are set equal to 1 so that \( p_l = \dot{q}_l \)). If local equilibrium holds, the definition of kinetic temperature stems from the local version of the “virial theorem” 
\[ \left\langle p_l \frac{\partial h_l}{\partial p_l} \right\rangle = \left\langle q_l \frac{\partial h_l}{\partial q_l} \right\rangle = T_l, \tag{6} \]
where \( \langle \cdot \rangle \) denotes the time average over a sufficiently long trajectory. Assuming, as it is indeed the case of our model, that Eq. (6) holds, we define 
\[ T_l = \left\langle p_l^2 \right\rangle. \tag{7} \]
The very definition of \( j_l \) is non-trivial in strongly anharmonic systems i.e. at high energies/temperatures. The correct way to proceed (see the Appendix and Ref. [13]) is to perform the spatial Fourier transform of Eq. (7) and to expand the result in powers of the wavenumber \( k \). Neglecting all higher-order terms, as it is usually done in hydrodynamics, one eventually obtains that the heat flux at the \( l \)-th position is given by
\[ j_l(t) = \frac{1}{2} a p_l (f_{l+1} + f_l), \tag{8} \]
so that \( p_l f_{l+1} \) has the simple interpretation of the flow of potential energy from the \( l \)-th to the neighbouring particle. In the simulations, we have measured the time average \( \langle j_l \rangle \) in the bulk. Notice that the stationarity condition implies \( \langle p_l f_{l+1} \rangle = \langle p_l f_l \rangle \), as it can be easily derived from the condition \( \langle \dot{q}_l \rangle = 0 \).

For later convenience we define the total flux through a chain or a subchain of \( N \) particles, as the integral of \( j(x, t) \), namely
\[ J(t) = \frac{1}{N} \sum_l j_l(t). \tag{9} \]
At equilibrium, the instantaneous fluxes fluctuate “randomly” around zero.

IV. MACROSCOPIC PROPERTIES IN THE NONEQUILIBRIUM STATE

Here, we describe the outcome of our molecular-dynamics simulations, performed with fixed values of the temperatures \( T_R \) and \( T_L \). With this setting, larger numbers of particle correspond to smaller temperature gradients (i.e. small external fields), so that, for \( N \to \infty \), equilibrium dynamics is locally approached along the chain. In other words, we are considering cases where the usual linear response or Green-Kubo theory is eventually applicable. Nevertheless, the problem remains highly nontrivial and deserves, as we will see, much attention.

The numerical simulations have been performed with several values of \( N \) up to 4096, monitoring both the kinetic temperatures and the heat fluxes. In every case, after a suitably long transient, the system reaches a statistically stationary state, where each oscillator is in local equilibrium at a certain kinetic temperature and Eq. (3) is well verified.

A. The temperature field

Whenever the imposed temperatures are different from one another, the microscopic dynamics corresponds to a nonequilibrium macrostate characterized by a nonuniform temperature field along the chain (see Fig. 1).
FIG. 1. Temperature profiles with $T_L = 152$, $T_R = 24$, $\Theta = 1$, for different lattice lengths. Note that a nonlinear profile sets in for the larger $N$ values. For $N = 66$ we report the temperature fields for two other values of the response time, namely $\Theta = 0.1$ (dashed line) and $\Theta = 10$ (dot-dashed line).

Long averaging reveals that the temperature gradient is rather smooth except at the boundaries, where thermal resistance effects may generate large temperature jumps. Such effects turn out to depend on the response time of the thermostats and are particularly relevant for small $\Theta$'s (see third panel in Fig. 1). One can understand this phenomenon by realizing that a fast reaction of the thermostats makes the dynamics of the end particles qualitatively different from that of the neighbouring ones. As one is interested in measuring the bulk contribution to the conductivity, it is important to minimize the boundary effects, i.e. the temperature gaps observed at both extrema. This implies that $\Theta$ should be chosen as large as possible; however, the larger is $\Theta$, the longer must last the simulations in order to have reliable statistics. We find that the choice $\Theta = 1$ represents a reasonable compromise.

As already observed in Ref. [2], the behaviour of the temperature profiles for different numbers of particles is well reproduced by the scaling Ansatz,

$$T_i = T(i/N)$$

i.e., the shape of the profile is independent of $N$, if the chain length is rescaled to 1. This implies that the temperature field scales everywhere in the same manner and one can choose equivalently any interval for measuring the temperature gradient (provided that the interval is measured in fractions of the total length).

The temperature profile in the bulk is not exactly linear (except for rather small $N$s), as one could expect from the stationary solution of the heat equation (namely the Fourier law). The nonlinearity of the profiles could at first be interpreted as an indication of a temperature-dependent conductivity, but this is actually not the case. In fact, simulations performed with as small temperature-differences as $T_L - T_R = 4$ and for $N = 128$, still reveal clear deviations from linearity.

\[^{\dagger}\]Similar problems arise also with random thermostats: ingenious tricks have been worked out to circumvent them [4].
FIG. 2. Behaviour of the thermal conductivity, Eq. (11), as a function of the lattice length $N$ for $T_L = 152$, $T_R = 24$. The flux $j$ is computed averaging over one long trajectory ($\approx 10^6$), started from random initial conditions and after discarding a transient ($\approx 10^4$). The inset shows the results of Ref. [14].

B. Thermal conductivity

Another relevant macroscopic feature is the onset of a constant, on average, heat flux, namely $\langle j_l \rangle = j$, for every $l = 2, \ldots, N - 1$ (the flux through the oscillators in contact with the heat reservoirs must account also for the energy exchange with each thermostat - see the following subsection).

The thermal conductivity is defined (to the lowest order in the applied gradient) as the ratio

$$\kappa = \frac{j}{dT/dx}.$$  \hspace{1cm} (11)

Our main result is that $j$, which vanishes as $N \to \infty$, approaches 0 more slowly than the temperature gradient, thus implying a diverging conductivity in the thermodynamic limit. In fact, the simulations do reveal that the heat flux scales as $j \propto N^{-\alpha}$, with $\alpha$ definitely smaller than 1. Accordingly (see Fig. 2), $\kappa$ diverges as $N^{1-\alpha}$, since the scaling behaviour of the profile implies that $dT/dx$ is proportional to $(T_L - T_R)/N$. A careful scrutiny of the data in Fig. 2 reveals a sort of crossover from $\alpha \approx 0.55$, for $N < 250$ to $\alpha \approx 0.62$ for larger numbers of particles.

It is worth mentioning that a similar behaviour of the conductivity is found also by using other thermostating schemes, such as stochastic interactions with a gas of Maxwellian particles. For comparison, in the inset of Fig. 2, we report the data taken from [14]. Although they refer to different temperatures ($T_L = 1500$, $T_R = 150$, if expressed with reference to the same value of $\beta$ here employed), the scaling behaviour is approximately the same as ours.

Therefore, we are forced to conclude that, at least for the considered system sizes, Fourier law is not satisfied and chaoticity is not sufficient to ensure its validity.

C. Entropy production

The energy flux at the chain ends is simply given by

$$j_{L,R} = -\langle \zeta_{L,R} Q_{L,R}^2 \rangle = -\langle \zeta_{L,R} \rangle T_{L,R},$$  \hspace{1cm} (12)

where the second equality is obtained from the condition $(dQ_{L,R}^2/dt) = 0$. In the stationary regime, the balance between the ingoing and outgoing fluxes implies that $j_L = -j_R$ which, in turn, implies that $\langle \zeta_L \rangle$ and $\langle \zeta_R \rangle$
must have opposite signs. This rather obvious relationship, stemming from energy conservation, has a somehow surprising meaning, if interpreted from the point of view of dynamical equations. In fact, a negative ⟨ζ_L⟩ (the flux must be obviously positive in the left-end, which is in contact with the hotter reservoir) means an expansion of volumes rather than a dissipation! The apparent anomaly is immediately clarified by noticing that the system in the whole is globally dissipative as γ = ⟨ζ_R + ζ_L⟩ turns out to be positive in all simulations that we have performed. This is also consistent with a theorem recently proven by Ruelle [15] for time-reversible systems and expresses the intuitive notion that if the energy is conserved on the average, it is not possible that volumes steadily diverge. What is not a priori trivial is that a finite dissipation spontaneously arises as soon as a non-equilibrium stationary state sets in [8,9].

Eq. (12) is also susceptible of an interpretation in terms of entropy production. By subtracting from one another the two expressions of the fluxes and noticing that j_L = j_R > 0, one obtains

⟨ζ_L⟩ + ⟨ζ_R⟩ = j \left( \frac{1}{T_R} - \frac{1}{T_L} \right) .

which can be interpreted as a balance relation for the global entropy production. In fact, according to the principles of irreversible thermodynamics, the local rate of entropy production σ in the bulk is given by

σ(x) = j \frac{d}{dx} \left( \frac{1}{T(x)} \right) .

Upon integrating Eq. (14), the r.h.s of Eq. (13) is obtained, which can thus be interpreted as the global production rate of entropy in the bulk. On the other hand, according to general arguments on reversible thermostats [8], the l.h.s. of Eq. (13) can be identified with the entropy production from the heat baths. Eq. (13) has been accurately verified in a wide range of temperatures.

V. CHAOTIC HYPOTHESIS AND LARGE FLUCTUATIONS

We now turn our attention to far-from-equilibrium regimes, where the applied gradient is very large, i.e., to the case of short chains with large temperature differences at the boundaries. Our aim is to check the validity of the fluctuation theorem, recently proposed by Gallavotti and Cohen [8], and carefully tested in a periodic Lorentz gas with an electric applied field [10]. The test is rather crucial for at least two reasons: (i) at variance with most of the cases considered in literature, here only the boundary particles are thermostatted [16]; (ii) it is not a priori clear that the chaotic hypothesis, one of the key assumptions for the validity of the theorem, applies to the present case. In fact, it is far from obvious that a dynamical system such as an FPU chain, displaying a slow convergence to equipartition at low temperatures, is “Anosov-like” in the thermodynamic limit.

The fluctuation theorem essentially connects the probability of positive to that of negative values of the entropy production. Although we recommend the reader to consult [8] for a detailed exposition of the theorem, here we summarize the main lines of the proof to give a flavour of the various steps. The starting observation is that any two regions in phase space, mutually related by the involution I, are characterized by opposite entropy values σ and −σ (the entropy changes sign upon applying the involution I). The second key point is that the existence of a Sinai-Ruelle-Bowen measure implies that the probability of one such region R is proportional to the product of the expanding multipliers (over a suitable time lag). As a consequence, invariance under time-reversal ensures that the probability to observe −σ in R is also proportional to the product of the inverse of the contracting multipliers in I(R). This fact implies that the ratio of the probability of observing σ to that of −σ can be reduced to the product of expanding and contracting multipliers, all taken at the point where σ is actually observed. This product is, in turn, nothing but the volume contraction or, equivalently, the exponential of the entropy production.

From Eq. (13), one can see that, apart from an irrelevant multiplicative constant (the external-field amplitude), the heat flux j is equivalent to the entropy production. In order to make the analogy with the previous study even more stringent, we have, however, preferred to consider the global heat flux as defined in Eq. (9) as the latter quantity corresponds to a spatial average over all oscillators (let us indeed recall that in many previous

§Technically speaking, we should refer to a sufficiently small element of a Markov partition.
studies the entropy production is an extensive quantity, proportional to the number of degrees of freedom). This change of definition does not affect the symmetry properties of $J$, so that the fluctuation theorem applies (or not) independently of this modification.

Therefore, our starting point is the finite-time average of the global heat flux (proportional to the entropy production),

$$\langle J \rangle_\tau = \frac{1}{\tau} \int_{t}^{t+\tau} J(t') dt' ,$$

where the average is performed over a sufficiently long trajectory to ensure a good accuracy of the underlying Markov approximation (see again Ref. [8]). We then compute the probability distribution $P_\tau$ of the variable

$$z = \frac{\langle J \rangle_\tau}{\langle J \rangle_\infty}$$

where $\langle J \rangle_\infty$, denoting the “infinite time” average of the global flux, coincides with the stationary average flux $j$ introduced in the previous sections. The Gallavotti-Cohen conjecture then reads as

$$\ln \frac{P_\tau(z)}{P_\tau(-z)} = \tau z j \left( \frac{1}{T_R} - \frac{1}{T_L} \right) .$$

We have performed simulations for $N = 14$, $T_L = 120$, $T_R = 56$, $\Theta = 1$ and several values of $\tau$ ranging from 5 to 80. At variance with the results of Ref. [10], the bell-shaped distribution $P(z)$ (Fig. 3) is clearly not Gaussian: both of its tails approach zero exponentially for large values of $|z|$, but with different rates. Upon increasing $\tau$, the central part of $P_\tau(z)$ approaches more and more a Gaussian shape as one would expect from the increasing statistical independence of the data. On the other hand, reliable numerical measures become more and more difficult: for instance, already for $\tau = 80$, negative values of $z$ are much too rare to permit the evaluation of the distribution over a reasonable integration time. Nevertheless, the linear behaviour predicted by Eq. (17) is indeed observed, as shown in Fig. 4, where the numerical points are superimposed to the theoretical prediction.

FIG. 3. The distribution $P_\tau(z)$ for different values $\tau$. The chain length is $N = 14$ and the boundary temperatures are $T_L = 120$, $T_R = 56$ and $\tau_0 = 50$. The value of the average flux is $j = 30.67 \pm 0.01$. 
VI. CONCLUSIONS AND PERSPECTIVES

In this paper we have shown that the fluctuation theorem recently proposed by Gallavotti and Cohen is successfully verified for a chain of FPU oscillators in contact with time-reversible thermostats at the boundaries. It is worth stressing that this is a very different context with respect to the ones previously considered in the literature. In this sense, our results definitely enforce the generality of this approach in describing the thermodynamics of nonequilibrium stationary states in terms of the Sinai-Bowen-Ruelle probability distribution.

Furthermore, we have found that heat conductivity appears to diverge in the thermodynamic limit. This is at variance with results obtained with reference to the so-called ding-a-ling model. The origin of the divergence of \( \kappa \) in FPU seems to be traceable to the existence of quasi-conserved long-wavelength modes supporting almost ballistic transport along the chain. Such a feature is indeed generic for Hamiltonian models with smooth nearest-neighbour coupling like FPU, but it is clearly absent in models such as ding-a-ling which cannot sustain long-wavelength modes.

We plan to proceed towards a more detailed comprehension of heat conduction by exploring the following routes:

- Dependence of transport properties on the physical settings; for example, by changing the number of particles in thermal contact with the reservoirs.
- Measurement of the thermal conductivity in the framework of Green-Kubo linear response theory with equilibrium simulations.
- Application of the same approaches to different models of nonlinear chains of oscillators, including the extension to two and three dimensions.

In particular, we want to stress the importance of the last point since it is not unlikely that macroscopic validity of the Fourier law is generally ensured only in some higher dimension. After all, statistical mechanics is full of phenomena that do depend on the dimensionality.
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APPENDIX A:

In this Appendix we determine the expression of the heat flux for a 1d chain, where the neighbouring particles interact via a generic nonlinear potential, such that the resulting equations of motion are of the form (6). For simplicity we assume that the chain is infinite.

Let us write the energy density and the flux as Fourier integrals

\[ \tilde{h}(k, t) = \int h(x, t) e^{-ikx} dx, \quad \tilde{j}(k, t) = \int j(x, t) e^{-ikx} dx, \]

so that Eq. (7) becomes

\[ \frac{d\tilde{h}}{dt} + ik \tilde{j} = 0. \]  

(A2)

We now rewrite the last equation, by splitting the heat flux into two different contributions

\[ \tilde{j} = \tilde{j}^{(1)} + \tilde{j}^{(2)}, \]  

(A3)

such that, by the explicitly computing the time-derivative of \( \tilde{H} \), it is recognized that

\[ \tilde{j}^{(1)} = \sum_{l} p_l h_l e^{-ikx_l}, \]  

(A4)

while

\[ -ik \tilde{j}^{(2)} = \sum_{l} h_l e^{-ikx_l} = \frac{1}{2} \sum_{l} f_l(p_l + p_{l-1})(e^{-ikx_l} - e^{-ikx_{l-1}}). \]  

(A5)

As we want to determine \( \tilde{j}^{(2)} \) to the lowest order in \( ik \), we expand the exponentials as

\[ e^{-ikx_l} - e^{-ikx_{l-1}} \approx e^{-ikx_l} \left( -ik(x_l - x_{l-1}) + \mathcal{O}(k^2) \right), \]  

(A6)

end then

\[ \tilde{j}^{(2)} \approx \frac{1}{2} \sum_{l} f_l(p_l + p_{l-1})(x_l - x_{l-1}) e^{-ikx_l}. \]  

(A7)

Summing the two terms and recalling the definition of \( j \), it can be realized that (after some further index manipulation)

\[ j_l = p_l h_l + \frac{1}{2}(q_l - q_{l-1})(p_l + p_{l-1})f_l + a \frac{1}{2} p_l(f_l + f_{l+1}). \]  

(A8)

With similar calculations, it can be shown that the first two terms in the r.h.s. correspond to order-\( k^2 \) terms in the Fourier expansion so that they can be neglected and Eq. (8) is finally obtained.
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