Fourier Law in Low-dimensional Systems

Roberto Livi [a,b]

[a]*Dipartimento di Fisica, via G. Sansone 1 I-50019 Sesto Fioentino, Italy*
[b] *INFM, INFN and INOA Florence, Italy*

Contents

1 Introduction

Non–equilibrium phenomena are ubiquitous in nature and characterize many aspects of the physical world, like atmospheric circulation, thermo–chemical reactions, glass formation, heat and electronic conduction, deposition and growth, relaxation processes etc. These phenomena occur in the presence of external forces driving the physical system out of its equilibrium conditions. Stationary states can be achieved when the effect of the driving force is balanced by dissipation mechanisms: despite fluctuations, the system evolves in time maintaining practically unchanged its average properties.

These lecture notes aim at providing the reader a survey on the problem of heat transport with a special focus on low-dimensional systems. In fact, they may exhibit peculiar properties, like diverging heat conductivity in the thermodynamic limit. For pedagogical reasons we discuss a collection of simple models which summarize some of the main aspects and questions. Mathematical rigour will be used as much as possible, but we shall be obliged to rely also upon approximate methods or numerics.

Historically, the first goal of the old kinetic theory was the definition of transport coefficients through phenomenological constitutive equations. The basic hypotheses of this macroscopic theory of transport phenomena are the assumption that fluxes are proportional to thermodynamic forces and that the system evolves close to equilibrium [1]. For instance, when dealing with energy transport in a solid one defines the thermal conductivity κ through the *Fourier law*

$$\mathbf{J} = -\kappa \nabla T \quad . \tag{1}$$

where the heat flux $\mathbf{J}$ is the amount of heat transported through the unit surface in unit time and $T(\mathbf{x}, t)$ is the local temperature. Such a phenomenological relation was first proposed in 1808 by J.B.J. Fourier as an attempt to explain the phenomenon of the Earth cooling - a problem that had raised a long and controversial debate inside the scientific community, faced with the need of explaining the thermal gradient present inside the Earth. Eq.(1) is assumed to be valid close to equilibrium. Actually , the very definition of the local energy flux $\mathbf{J}(\mathbf{x}, t)$ and temperature field $T(\mathbf{x}, t)$ relies, in turn, on the *local equilibrium hypothesis* i.e., on the possibility of defining a local temperature for a macroscopically small but microscopically large volume at each location $\mathbf{x}$ for each time t.

The ultimate goal of a complete theory of transport phenomena in matter would be to obtain equations like (1) from the microscopic approach of statistical-mechanics, a task which has revealed of formidable difficulty. A typical puzzling example concerns the theory of heat transport by lattice vibrations in insulating crystals. These lecture notes aim at surveying the many efforts made for constructing such a microscopic theory, up to some of the most recent achievements, that have opened promising perspectives for a consistent theoretical approach.

The first and most elementary attempt to give a microscopic foundation to Fourier law dates

back to Debye. By rephrasing the results of the kinetic theory for the (diluted) phonon gas, he obtained that the thermal conductivity should be proportional to $Cv\ell$ where C is the heat capacity and v, ℓ are the phonon mean velocity and free path, respectively. In 1929, R. Peierls further extended this idea and formulated a Boltzmann equation [2] that shows how anharmonicity is necessary to obtain genuine diffusion of the energy through the so-called *Umklapp* processes. Since then, the Boltzmann-Peierls approach became one of the cornerstones in the theory of lattice thermal conductivity. In particular, it allows to compute the temperature dependence of κ on temperature. On the other hand, in order to be predictive this approach has to assume the relaxation time approximation, which reintroduces a somehow phenomenological ingredient, unjustified on the basis of a purely microscopic theory.

From a more fundamental point of view, there are even more basic questions that go beyond the actual calculation of the transport coefficients. For instance, under which conditions is local equilibrium obtained? How can we guarantee that a unique nonequilibrium stationary state is attained in a physically accessible time ? In this respect, simple mathematical models are an invaluable theoretical playground where one can hope to give a more firm foundation and to understand more deeply the hypotheses underlying eq. (1). It should be stressed that this program is still nowadays far from being accomplished, at least from a mathematically rigorous point of view [3]. On the other hand, the combination of analytical calculations and numerical simulations has proved also recently to be quite successful for investigating many of those items.

As usual in theoretical physics, the guiding criterion of mathematical simplicity leads naturally to consider 1 or 2d lattices (i.e., chains or planes) of point atoms interacting with their neighbors trough nonlinear forces. The hope is to reproduce realistic thermodynamic properties of their three-dimensional counterparts. This brings to the fore the following question: what are the minimal requirements for such model to satisfy or not eq. (1)? Although it may appear surprising, this issue has been addressed in the literature already in the late 60s without receiving a definite answer. As known in the context of fluids [4], much of the difficulties arise from the fact that transport coefficients in low spatial dimensions may not exist at all, thus implying a breakdown of standard hydrodynamics. In the context of insulating solids, this usually shows up as *(i)* a slow decay of equilibrium correlations of the heat current; *(ii)* a divergence of the *finite-size* conductivity $\kappa(N, T)$ in the thermodynamic limit $N \to \infty$ (where N is the number of atoms in the sample). One of our concerns in these lectures will be to clarify, through the analysis of some examples, under which conditions this may occur. We shall also comment about the possible universality of such a divergency.

Up to now we have been mainly emphasizing the theoretical issues that motivate the study of transport in low-dimensional lattice models. Of course, a further relevant motivation is the existence of a variety of real systems that could be, at least in principle, effectively described by 1 or 2d models. For instance, reduced dimensionality has been indeed invoked to explain experiments on heat transport in anisotropic crystals [5,6] or magnetic systems [7]. Remarkably, a dependence of thermal conductivity on the chain length of solid polymers has also been experimentally observed [8]. More generally, modern experimental techniques [9] allow to directly probe the transport properties of semiconductor films [10,11] and single-walled nanotubes [12,13] that markedly display one-dimensional features at low temperatures. Some theoretical

investigations of thermal conductance for a quantum wire in ballistic [14] and anharmonic [15] regimes have been also recently undertaken.

2   Heat conduction in harmonic chains

Harmonic chains is the class of systems where heat transport can be studied explicitly by analytic calculations. In fact, the crucial feature of harmonic chains is integrability, that yields the possibility of decomposing the heat flux into the sum of independent contributions associated with the various eigenmodes. Even if such models are quite far from real solids, they are useful for clarifying several aspects of heat conductivity. In particular, we are going to show that their study is very helpful also for clarifying the role of boundary conditions.

We first discuss the simplest case of a homogeneous chain: we shall obtain an analytic expression of the invariant measure for arbitrary coupling strength.

The effect of disorder is studied in the subsequent section, where the relevant quantities are described by perturbative calculations. For completeness, we shall also recall the localization properties of the eigenfunctions and self-averaging properties of several observables, such as the temperature profile and the heat flux. The approach that we are going to follow is mainly based on the Fokker-Planck equation and on simple stochastic calculus. An important alternative approach based on transmission coefficients can be found in [16].

The homogeneous harmonic chain - Let us consider a homogeneous harmonic chain with fixed boundary conditions in contact with stochastic Langevin heat baths. The equations of motion read

$$\ddot{q}_n = \omega^2(q_{n+1} - 2q_n + q_{n-1}) + \delta_{n1}(\xi_+ - \lambda\dot{q}_1) + \delta_{nN}(\xi_- - \lambda\dot{q}_N), \tag{2}$$

where $\xi_\pm$ are independent Wiener processes with zero mean and variance $2\lambda_\pm k_B T_\alpha$, with $T_+ > T_-$. In order to lighten the notation we have assumed unitary masses. This set of stochastic equations can be solved [17] by passing to a phase-space description, i.e., by writing down the Liouville equation that corresponds to the following Fokker-Planck equation

$$\frac{\partial P}{\partial t} = A_{ij}\frac{\partial}{\partial x_i}(x_j P) + \frac{D_{ij}}{2}\frac{\partial^2 P}{\partial x_i \partial x_j} \tag{3}$$

Here and in the following we adopt the convention of implicit summation over repeated indices; $x_i = q_i$ for $1 \le i \le N$, $x_i = \dot{q}_i$ for $N < i \le 2N$. A_{ij} and D_{ij} are elements of the $2N \times 2N$ matrices $\mathbf{A}$ and $\mathbf{D}$ that we write in terms of $N \times N$ blocks

$$\mathbf{A} = \begin{pmatrix} \mathbf{0} & -\mathbf{I} \\ \omega^2\mathbf{G} & \lambda\mathbf{R} \end{pmatrix} \quad , \quad \mathbf{D} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & 2\lambda k_B T(\mathbf{R} + \eta\mathbf{S}) \end{pmatrix} \tag{4}$$

where we have introduced the average temperature $T = (T_+ + T_-)/2$ and the rescaled temperature difference $\eta = (T_+ - T_-)/T$. Moreover, $\mathbf{0}$ and $\mathbf{I}$ are the null and identity matrices, $\mathbf{G}$ is a tridiagonal matrix defined as

$$G_{ij} = 2\delta_{ij} - \delta_{i+1,j} - \delta_{i,j+1} \quad ,$$

while $\mathbf{R}$ and $\mathbf{S}$ are defined as

$$
\begin{aligned}
R_{ij} &= \delta_{ij}(\delta_{i1} + \delta_{iN}), \\
S_{ij} &= \delta_{ij}(\delta_{i1} - \delta_{iN})
\end{aligned}
\tag{5}
$$

The general solution of this equation is

$$P(x) = \frac{\text{Det}\{\mathbf{C}^{-1/2}\}}{(2\pi)^N} \exp\left[-\frac{1}{2}C_{ij}^{-1}x_i x_j\right] \tag{6}$$

where $\mathbf{C}$ is the symmetric covariance matrix

$$C_{ij} \equiv \langle x_i x_j \rangle \equiv \int dx P(x) x_i x_j \tag{7}$$

By replacing the definition of $\mathbf{C}$ into eq. (3), one finds that

$$\dot{\mathbf{C}} = \mathbf{D} - \mathbf{AC} - \mathbf{CA}^\dagger \tag{8}$$

where $\mathbf{A}^\dagger$ is the transpose of $\mathbf{A}$. Accordingly, the asymptotic stationary solutions can be determined from the equation [18]

$$\mathbf{D} = \mathbf{AC} + \mathbf{CA}^\dagger \tag{9}$$

In order to solve the problem, let us write $\mathbf{C}$ in terms of $N \times N$ blocks,

$$\mathbf{C} = \begin{pmatrix} \overline{\mathbf{U}} & \overline{\mathbf{Z}} \\ \overline{\mathbf{Z}}^\dagger & \overline{\mathbf{V}} \end{pmatrix} \tag{10}$$

where the matrices $\overline{\mathbf{U}}$, $\overline{\mathbf{V}}$, and $\overline{\mathbf{Z}}$ express the correlations among positions and velocities,

$$\overline{U}_{ij} = \langle q_i q_j \rangle \quad , \quad \overline{V}_{ij} = \langle \dot{q}_i \dot{q}_j \rangle \quad , \quad \overline{Z}_{ij} = \langle q_i \dot{q}_j \rangle \quad , \tag{11}$$

If the temperatures of the two heat baths coincide (i.e., $\eta = 0$), it can be easily seen that

$$\mathbf{U}_e = \frac{k_B T}{\omega^2}\mathbf{G}^{-1} \quad , \quad \mathbf{V}_e = k_B T \, \mathbf{I} \quad , \quad \mathbf{Z}_e = 0 \tag{12}$$
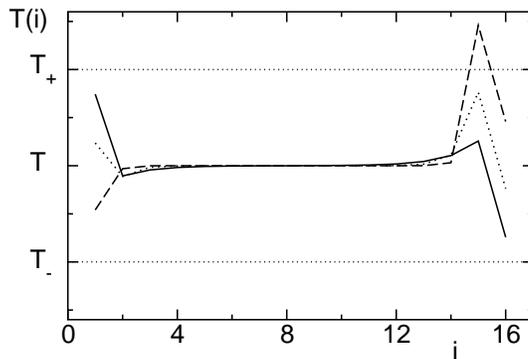
Fig. 1. The temperature profile for the harmonic chain, formula (13), for coupling parameter $\nu = 0.2$, 1.0 , 5.0 (solid, dotted and dashed lines respectively).

represents a meaningful solution, since it coincides with the equilibrium Boltzmann distribution $P(x) \approx \exp -H/k_B T$.

The derivation of the stationary solution in the out-of-equilibrium case is reported in Appendix 1 . All relevant correlations can be expressed in terms of the function $\phi(j)$ (see eq. (111)) that decays exponentially with the rate α defined in eq. (110). Direct inspection of correlations indicates that α measures the length over which the boundary reservoirs significantly affect the chain dynamics. As expected, α diverges in the weak coupling limit ($\nu = \omega^2/\lambda^2 \to \infty$).

From eqs. (106,108), it follows that position-position and velocity-velocity correlations are equal for all pairs of particles (i, j) such that $i + j$ is constant. The qualitative explanation of this property relies on the exponential decay of the boundary effects. In fact, the amplitude of, e.g., $\langle q_i q_j \rangle$ decreasing exponentially with both i and j has to depend on $i + j$. Less obvious is the left-right antisymmetry ($V_{ij} = V_{N-i+1,N-j+1}$) which implies that the boundary effects are exactly the same for the two thermostats, whatever is their temperature. This is nicely reproduced by the temperature profile

$$T_i = T(1 + \eta V_{ii}) = \begin{cases} T_+ - \nu \eta T \phi(1) & i = 1 \\ T[1 - \eta \nu \phi(2i - 1)] & 1 < i \leq N/2 \\ T[1 + \eta \nu \phi(2(N - i) - 1)] & N/2 < i < N \\ T_- + \nu \eta T \phi(1) & i = N \end{cases} \tag{13}$$

which exhibits a further unexpected property (see Fig. 1): the temperature is higher in the vicinity of the coldest reservoir (the only exception being represented by the first and last particles)!. Because of the exponential decay of $\phi(i)$, in the bulk, the temperature profile is constant as if the system were at equilibrium with temperature T. However, this is only superficially true, as position-velocity correlations significantly differ from the equilibrium ones.

Also the stationary local heat flux can be computed explicitly:

$$J_i = \omega^2 \overline{Z}_{i-1,i} = \frac{\omega^2 k_B T \eta}{\lambda} \phi(1) \ . \tag{14}$$

6

Eq. (103) implies that the value of $Z_{i,j}$ depends on $i - j$ rather than on $i + j$, as before. Physically, this symmetry implies that in the stationary state J_i must be independent on the lattice position i. In the large N limit, eqs. (110,111) yield

$$J = \frac{\omega^2 k_B T}{2\lambda} \left[1 + \frac{\omega^2}{2\lambda^2} - \frac{\omega}{\lambda} \sqrt{\frac{\omega^2}{4\lambda^2} + 1} \right] (T_+ - T_-). \tag{15}$$

Accordingly, the heat flux is proportional to the temperature difference rather than to the gradient as it should be if the Fourier law would be satisfied. This proves that **homogeneous harmonic chains do not exhibit normal transport properties**.

For what concerns the dependence of the flux on λ, we see that J vanishes both in the limit of large and small couplings. The asymptotic expressions are

$$J = \begin{cases} \frac{\omega^2}{2\lambda} k_B (T_+ - T_-) & \lambda \gg \omega \\ \frac{\lambda}{2} k_B (T_+ - T_-) & \lambda \ll \omega \end{cases}, \tag{16}$$

The maximum flux is attained for $\lambda/\omega = \sqrt{3}/2$, a value that is close to the one observed numerically in the nonlinear cases.

We conclude this section by recalling that a similar procedure can be adopted for solving the problem of heat baths characterized by stochastic elastic collisions. In Ref. [17], it is shown that very similar expressions are obtained also in this case, with only minor quantitative differences in the numerical factors. Furthermore, it is worth mentioning the model of self-consistent reservoirs introduced in [19], which can be solved exactly.

3 Heat conduction in disordered harmonic chains

Now we aim at considering the role of disorder on transport properties by studying the random-mass (or isotopically disordered) chain

$$m_n \ddot{q}_n = q_{n+1} - 2q_n + q_{n-1} \quad . \tag{17}$$

Boundary conditions play a crucial role, but for the moment we leave them unspecified (see below). Let us also mention the general results by Lebowitz and collaborators [20,21]: they have shown rigorously that the system approaches a unique stationary nonequilibrium state for a large class of heat baths.

As it is known since Anderson's pioneering contributions, the presence of disorder generally induces localization of the normal modes of the chain. As a consequence, one should expect that it behaves as a perfect thermal insulator. Nonetheless, the actual situation turns out to
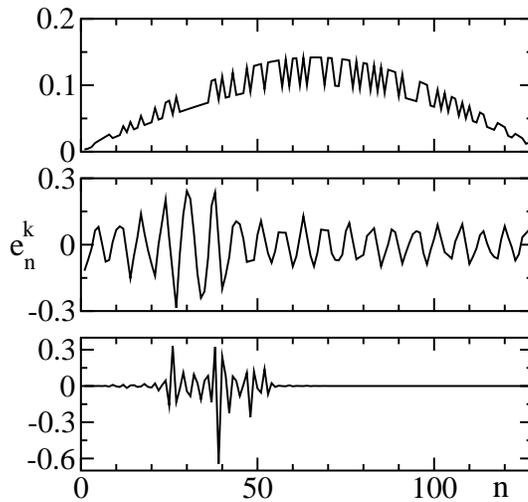
Fig. 2. The first, 41st and 100th eigenvector (from top to bottom) in a chain of 130 particles with random masses with an even distribution of 1 and 1/2 values. The increasing localization with increasing eigenvalue is evident.

be much more complicated, depending on boundary conditions and on the properties of the thermostats.

Localization of the eigenmodes - Let us first recall some useful basic facts about localization. For illustration, we consider the example of a disordered chain with two evenly-distributed types of particles. Some of the numerically computed eigenvectors are shown in Fig. 2. Upon ordering them with increasing eigenfrequencies, a distinct difference in their localization properties can be recognized. Indeed, for small frequencies (upper panel of Fig. 2), randomness induces only a relatively weak modulation of the amplitude; a partial localization can be recognized in the intermediate panel, while a clear evidence of localization is visible only for the high-frequency eigenvector, reported in the bottom panel.

The application of the transfer matrix formalism to the eigenvalue equation allows for a rigorous investigation of the problem at hand. After inserting the expression $q_n = v_n e^{i\omega t}$ in eq. (17), we obtain

$$-m_n \omega^2 v_n = v_{n-1} - 2v_n + v_{n+1}. \tag{18}$$

It is well known that the spectral properties of linear operators involving the discrete Laplacian can be determined from a recursive equation for the new variable $R_n = v_n/v_{n-1}$. The most known example where this approach has been successfully employed is that of Anderson's quantum localization in the tight-binding approximation. In the present context, eq. (18) yields

$$R_{n+1} = 2 - m_n \omega^2 - \frac{1}{R_n}, \tag{19}$$

an equation that can be interpreted as a "discrete time" stochastic equation. The mass m_n plays the role of a noise source (with bias), whose strength is gauged by the frequency ω. In

8

particular, the inverse localization length γ is given by

$$\gamma = \langle \ln |R_n| \rangle, \tag{20}$$

while the integrated density of states $I(\omega)$ follows from node counting arguments, i.e., $I(\omega) = f$, where f is the fraction of negative R_n values. In Fig. 3 it is shown that I increases linearly for small ω and exhibits some irregular fluctuations at larger frequencies. The upper band edge (at $\omega \simeq 2.8$) is easily identifiable as the point above which $I(\omega)$ remains constant and equal to one. At variance with the standard Anderson's problem, where all eigenmodes are exponentially localized, here $\gamma \to 0$ for $\omega \to 0$. This can be easily understood from equation (19): Since ω^2 multiplies the stochastic term, disorder becomes less and less relevant in the small frequency limit. In this limit, one can thus resort to a perturbative approach. Let us start noticing that for $\omega = 0$, $R = 1$ is a marginally stable fixed point of the recursive equation (19). For small ω, an intermittent process sets in: after a slow drift driving R_n below one, a reinjection to values larger than one occurs and nonlinearity become suddenly relevant. The process repeats again and again. By writing $R_n = 1 + r_n$ and expanding in powers of r_n, we find that the dynamics in the vicinity of $R_n = 1$ is described by

$$r_{n+1} = r_n - r_n^2 - \omega^2 \langle m \rangle + \omega^2 \delta m \tag{21}$$

where we have included only the first nonlinear correction and written separately the average value of the noise term. In the limit of small ω, this equation can be approximated by the Langevin equation

$$\dot{r} = -r^2 - \omega^2 \langle m \rangle + \omega^2 \delta m \tag{22}$$

where, for the sake of simplicity, the same notations have been kept. The corresponding Fokker-Planck equation writes

$$\frac{\partial P}{\partial t} = \frac{\partial (r^2 + \omega^2 \langle m \rangle) P}{\partial r} + \omega^4 \frac{\sigma_m^2}{2} \frac{\partial^2 P}{\partial r^2} \tag{23}$$

where $\sigma_m^2 = \langle m^2 \rangle - \langle m \rangle^2$ stands for the variance of the mass distribution. Given the steady incoming and outcoming flow, the stationary solution can obtained by imposing

$$(r^2 + \omega^2 \langle m \rangle) P + \omega^4 \frac{\sigma_m^2}{2} \frac{dP}{dr} = C \tag{24}$$

where C represents the probability flux to be determined by imposing the normalization of the probability density P. Notice also that C can be identified with the integrated density of states $I(\omega)$, since it corresponds to the probability that, at each iterate, R_n is reinjected to the right,
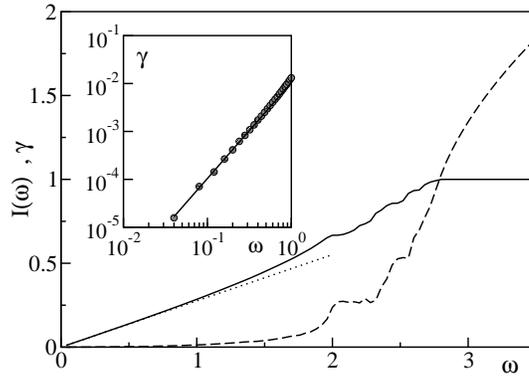
9

Fig. 3. Integrated density of states, $I(\omega)$ (solid line), and inverse localization length, γ (dashed line), as a function of the frequency ω for a chain with mass disorder: the particles have either mass 1 or 1/2 with equal probability. The dotted line corresponds to the analytic expression (25). In the inset the inverse localization length is plotted in doubly logarithmic scales (circles) and compared with the theoretical formula (28) - solid line.

i.e., the probability of having a node in the eigenvector. In the absence of disorder ($\sigma_m = 0$),

$$I(\omega) = C = \frac{\sqrt{\langle m \rangle}}{\pi} \omega \qquad (25)$$

and, correspondingly,

$$P_0(r) = \frac{1}{\pi} \frac{\omega \sqrt{\langle m \rangle}}{r^2 + \omega^2 \langle m \rangle} \qquad (26)$$

This approximation is already sufficient to reproduce the behavior of $I(\omega)$ at small frequencies, as in the limit of $\omega \to 0$ the variance of the disorder goes to zero faster than the average value. This is confirmed by comparing the dotted line in Fig. 3 (corresponding to the analytic expression (25)) with the numerically determined integrated density.

On the other hand, the above approximation is not accurate enough to determine the localization length, as disorder is totally disregarded. Indeed, the symmetry of P_0 implies that $\gamma \approx \langle r \rangle = 0$. We have to go one step further by writing $P(r)$ as P_0 plus a small perturbation. A simple calculation shows that

$$P(r) = P_0(r) + \frac{\omega^5 \sigma_m^2 r \sqrt{\langle m \rangle}}{\pi (r^2 + \omega^2 \langle m \rangle)^3} \qquad (27)$$

From expression (20) for the inverse localization length γ, we find that

$$\gamma = \langle r \rangle = \frac{\omega^2 \sigma_m^2}{8 \langle m \rangle}, \qquad \text{for} \qquad \omega \longrightarrow 0 \qquad (28)$$
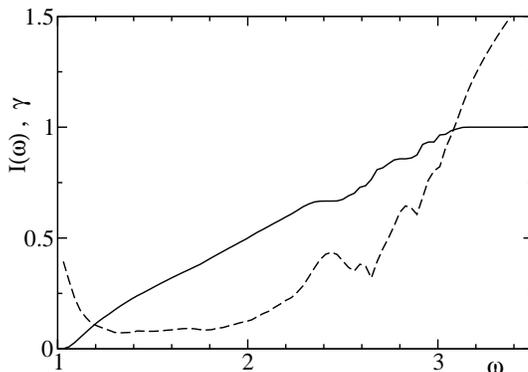
10

Fig. 4. Integrated density of states, $I(\omega)$ (solid line), and inverse localization length, γ (dashed line) for a random-mass chain as in Fig. 3 with the addition of a unit frequency on-site potential.

an equation derived in Ref. [22] (see Fig. 3).

If we add a harmonic on-site potential to eqs. (17), the corresponding scenario becomes analogous to that of the 1d Anderson's problem with all eigenfunctions being exponentially localized. This is illustrated in Fig. 4 where we have added harmonic springs with unit constant (i.e., a force term $-q_n$ acting on the n-th particle) to the chain with random masses considered above. The lower band-edge is now strictly bounded away from zero and the inverse localization length does not vanish.

The temperature profile - In order to study the nonequilibrium properties, we need to include the coupling with the thermal reservoirs. Here below, we consider Langevin-type heat baths, as they allow an analytic treatment though limited to the weak-coupling regime. The starting equation writes

$$m_n \ddot{q}_n = q_{n+1} - 2q_n + q_{n-1} + \delta_{n1}(\xi_+ - \lambda \dot{q}_1) + \delta_{nN}(\xi_- - \lambda \dot{q}_N) \qquad (29)$$

where, for simplicity, we have assumed $\lambda_+ = \lambda_- = \lambda$. Although the equations are still linear, there is no general method to derive an analytic solution for generic values of the coupling constant λ. Accordingly, we restrict ourselves to consider the perturbative regime $\lambda \ll 1$. It is convenient to introduce the new variable

$$u_n = \sqrt{m_n} q_n \quad , \qquad (30)$$

which allows rewriting eq. (29) as

$$\ddot{u}_n = \frac{u_{n+1}}{\sqrt{m_n m_{n+1}}} - 2\frac{u_n}{m_n} + \frac{u_{n-1}}{\sqrt{m_n m_{n-1}}} +$$
$$\frac{\delta_{n1}}{m_1}(\sqrt{m_1}\xi_+ - \lambda \dot{u}_1) + \frac{\delta_{nN}}{m_N}(\sqrt{m_N}\xi_- - \lambda \dot{u}_N) \ , \qquad (31)$$

The advantage of this representation is that the operator describing the bulk evolution is symmetric and, accordingly, can be diagonalized by an orthogonal transformation. In other

11

words, upon denoting with e_n^k the nth component of the kth eigenvector, it turns out that $\sum_n e_n^k e_n^h = \delta_{kh}$ and $\sum_k e_n^k e_j^k = \delta_{nj}$.

With reference to the new variables $U_k = \sum_n u_n e_n^k$, the equations of motion write as

$$\ddot{U}_k = -\omega_k^2 U_k - \lambda \sum_j C_{kj} \dot{U}_j + \frac{e_1^k}{\sqrt{m_1}}\xi_+ + \frac{e_N^k}{\sqrt{m_N}}\xi_- \tag{32}$$

where $-\omega_k^2$ is the real, negative kth eigenvalue of the unperturbed evolution operator and

$$C_{kj} = \frac{e_1^k e_1^j}{m_1} + \frac{e_N^k e_N^j}{m_N} \quad . \tag{33}$$

eqs. (32) show that the normal modes are coupled among themselves through the interaction with the reservoirs. Standard stochastic calculus applied to the modal energy $E_k = (\dot{U}_k^2 + \omega_k^2 U_k^2)/2$ shows that the stationarity condition for the time average $\langle \dot{E}_k \rangle = 0$ implies

$$C_{kk}\langle \dot{U}_k^2 \rangle + \sum_{j \neq k} C_{kj}\langle \dot{U}_k \dot{U}_j \rangle = T_+ \frac{(e_1^k)^2}{m_1} + T_- \frac{(e_N^k)^2}{m_N}. \tag{34}$$

Now, we want to show that this sum is negligible in the small-coupling limit. In fact, from the equality

$$\frac{d\langle \dot{U}_k U_h \rangle}{dt} = 0, \tag{35}$$

we find that

$$\langle \dot{U}_k \dot{U}_h \rangle - \omega_k^2 \langle U_k U_h \rangle - \lambda \sum_j C_{jh}\langle \dot{U}_j U_h \rangle = 0 \tag{36}$$

By solving this equation together with the symmetric expression obtained by exchanging k and h, one obtains that $\langle \dot{U}_k \dot{U}_h \rangle$ is proportional to λ for $k \neq h$. Accordingly, up to first order in λ,

$$\langle \dot{U}_k^2 \rangle = \frac{1}{C_{kk}}\left(T_+ \frac{(e_1^k)^2}{m_1} + T_- \frac{(e_N^k)^2}{m_N} \right), \tag{37}$$

As a consequence, by neglecting first order corrections, the local temperature T_n reads

$$T_n = \left\langle \left(\sum_k \dot{U}_k e_n^k \right)^2 \right\rangle \approx \sum_{k=1}^N \frac{(e_n^k)^2}{C_{kk}}\left(T_+ \frac{(e_1^k)^2}{m_1} + T_- \frac{(e_N^k)^2}{m_N} \right) \tag{38}$$
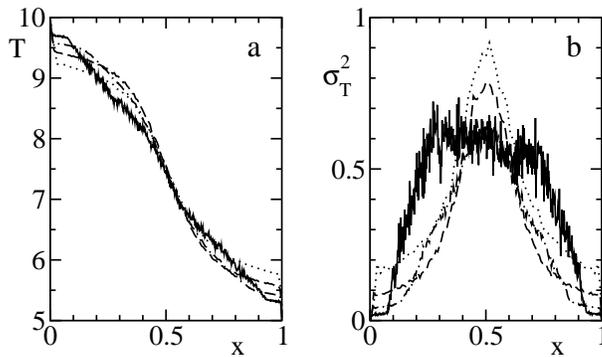
12

Fig. 5. (a) The disorder-averaged temperature profile as predicted from the formula (38) for different chain lengths (dotted, dashed, dot-dashed and solid curves refer to $N = 64, 128, 256$, and 512 respectively). (b) The variance of the temperature in the same notations as in panel (a).

This is basically the expression derived by Matsuda and Ishii [22]. As a consistency check, one can easily verify that if $T_+ = T_- = T$, the local temperature T_n is equal to T for all values of n (this follows from the normalization condition on the eigenvectors). Furthermore, the profile is flat also when $T_+ > T_-$ and the amplitude of all eigenvectors is the same at the two chain-ends: in this case, $T_n = (T_+ + T_-)/2$. An obvious limiting case is the homogeneous chain. Generally speaking, even though the dynamics of a generic disordered chain is statistically invariant under left-right symmetry, the same does not hold true for each individual eigenvector.

Visscher [23] challenged equation (38) by arguing that quasi-resonances could be generic enough to affect typical realizations of the disorder. In fact, a crucial assumption in the derivation of the expression for the temperature profile is that cross-correlations in eq. (38) are negligible. This is basically correct, unless pairs of frequencies are sufficiently close to each other, in which case the resonance phenomena should be properly taken into account. Visscher indeed discussed particular examples of mass distributions, where a more refined theory is needed. However, as long as we are interested in generic realizations, the problem is whether quasi-degeneracies in the spectrum are sufficiently frequent to significantly affect the overall validity of formula (38). In all the cases we have considered this issue turned out to be practically irrelevant.

Formula (38) does not allow to obtain an analytic form of the profile since it requires the knowledge of the eigenvectors and, on the other hand, the localization length alone does not suffice to predict their amplitude at the boundaries. Therefore, numerical diagonalization of the Hamiltonian for each different realization of the disorder is required. In Fig. 5a we have plotted the disorder-averaged profile as a function of the rescaled lattice position $x = n/N$. Upon increasing the chain length, the profile seems to slowly attain a linear shape, but sizeable deviations are still present for chains as long as $N = 512$. Such slow convergence is confirmed in Fig. 5b, where we plotted the sample-to-sample variance σ_T^2 of the temperature field. Although its asymptotic behavior is even less clear, it is at least evident that fluctuations do not vanish in the thermodynamic limit. This is tantamount to saying that the temperature profile is not a self-averaging quantity.

Such difficulties dramatically emerge when performing direct simulations of a disordered chain. This issue is of great practical importance also in view of more complex models, where analytical

13

results are not available. The major problem is represented by the extremely slow convergence towards the asymptotic regime that can be explained as follows. Eq. (32) shows that the effective coupling of each eigenmode with the reservoirs is proportional to its square amplitude at the extrema. Therefore, all eigenmodes that are localized away from the boundaries can thermalize only in astronomically long times. To be more specific, the coupling strength of an eigenmode characterized by an inverse localization length γ is of order $\exp(-\gamma N)$, since it is localized a distance equal, on the average, to the half of the chain length. This implies that the asymptotic profile is attained over times that grow exponentially with N. In other words, the stationary state is never reached in the thermodynamic limit.

Heat flux - In the case of stochastic heat baths (like those considered in the previous section) and under stationary conditions the average heat flux can be obtained directly from the temperature profile. In fact, the average amount of energy exchanged between the first particle ($n = 1$) and the heat reservoir at temperature T_+ is given by the expression the relation

$$J(\lambda, N) = \frac{\lambda}{m_1}(T_+ - T_1) \tag{39}$$

An equivalent expression holds at the opposite boundary, where the N-th particle is in contact with the heat reservoir at temperature T_-. By use of eq. (38) we obtain [22,23]

$$J(\lambda, N) = \lambda(T_+ - T_-)\sum_k \frac{(e_1^k)^2(e_N^k)^2}{m_N(e_1^k)^2 + m_1(e_N^k)^2} \equiv \sum_k J_k \tag{40}$$

where the k-th addendum J_k is naturally interpreted as the contribution of the k-th mode. The latter is larger for modes that have larger amplitudes at the boundaries and couple thus more strongly with the reservoirs. This interpretation can be justified from eqs. (32). Indeed, in so far as cross-coupling can be neglected, the dynamics of the kth eigenmode is approximately described by the equation

$$\ddot{U}_k = -\omega_k^2 U_k - \lambda C_{kk}\dot{U}_k + \frac{e_1^k}{\sqrt{m_1}}\xi_+ + \frac{e_N^k}{\sqrt{m_N}}\xi_-. \tag{41}$$

Standard stochastic calculus shows that, in the stationary regime, the energy exchanged per unit time with the two thermal baths is equal to J_k, where J_k coincides with the expression implicitly defined by eq. (40).

However, heat transport is characterized by more subtle mechanisms than one could infer from this simple picture of independent modes. This is immediately understood if we look at the general expression for the local heat flux, that, in the case of harmonic chains, reduces to

$$\langle j_n \rangle = -\langle q_n \dot{q}_{n+1} \rangle. \tag{42}$$

By expanding q_n and $\dot{q}_{n+1}$ in eigenmodes, this equation can be rewritten as

$$\langle j_n \rangle = - \sum_{k,h=1}^{N} \frac{e_{n+1}^k e_n^h}{\sqrt{m_n m_{n+1}}} \langle U_k \dot{U}_h \rangle, \tag{43}$$

an expression that, in spite of the explicit presence of the subscript n, is independent of n. The interesting point that is made transparent by this formula is that a nonvanishing flux is necessarily associated with the existence of **correlations among different modes**. This is all the way more meaningful, once we realize that diagonal terms with $k = h$ vanish, being $\langle U_k \dot{U}_k \rangle$ the average of the derivative of a bounded function. This observation seems to be in contrast with the derivation of Matsuda-Ishii formula itself, that is basically obtained by treating all modes as evolving independently of each other. Anyway, we should notice that the heat-flux is proportional to λ and this is compatible with the existence of weak modal correlations. In fact, "velocity-velocity" or "position-velocity" correlations may arise from the fact that all eigenmodes are subject to the same noise source (except for a multiplicative factor) and this may well induce a sort of **synchronization** among them.

Here below, we proceed with our perturbative analysis by deriving an analytic expression. Let us start by noticing that the equality $d\langle U_k U_h \rangle / dt = 0$ implies that

$$\langle \dot{U}_k U_h \rangle = -\langle \dot{U}_h U_k \rangle . \tag{44}$$

This antisymmetry property together with the further equality $d\langle \dot{U}_k \dot{U}_h \rangle / dt = 0$ imply that

$$\lambda C_{kh} \left(\langle \dot{U}_k^2 \rangle + \langle \dot{U}_h^2 \rangle \right) - \left(\omega_k^2 - \omega_h^2 \right) \langle \dot{U}_k U_h \rangle = 2\lambda \left(T_+ \frac{e_1^k e_1^h}{m_1} + T_- \frac{e_N^k e_N^h}{m_N} \right) \tag{45}$$

After replacing the expression of $\langle \dot{U}_k^2 \rangle$ (see eq. (37)) in the above equation, the latter can be solved for $\langle \dot{U}_k U_h \rangle$.

Instead of discussing the general case, we prefer to illustrate the presence of these correlations in the simple case of a homogeneous harmonic chain. In this context, one can, in principle, obtain a general expression for the correlations by transforming eq. (103) (derived for an arbitrary λ value) in k space. However, the calculations, though straightforward, are rather tedious. Therefore, we limit ourselves to considering the weak-coupling limit. The symmetry of the eigenmodes imply that if $\delta = h - k$ is an even number correlations vanish, while for an odd δ we have

$$\langle \dot{U}_k U_{k+\delta} \rangle = 2 \frac{\lambda(T_+ - T_-)}{m} \frac{e_1^k e_1^{k+\delta}}{\omega_{k+\delta}^2 - \omega_k^2} \tag{46}$$

In Fig. 6a we report the numerical results for a chain of length $N = 128$ with fixed boundary conditions and interacting with two thermal baths at temperatures $T_+ = 75$ and $T_- = 25$.
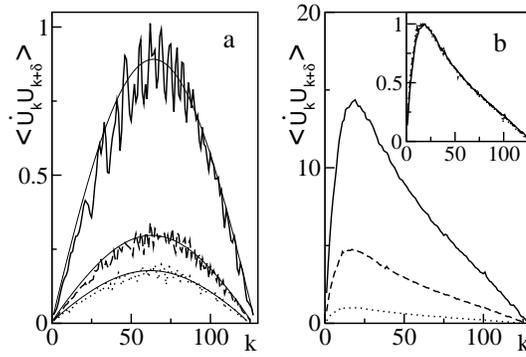
Fig. 6. Modal correlations for a harmonic chain of length $N = 128$ with fixed boundary conditions. Averaging has been performed on a time $t = 10^8$ units. Solid, dashed and dotted curves correspond to $\delta = 1$, 3, and 5, respectively, while the thin lines correspond to the analytic expressions (46). (a) refers to a weak-coupling case: the times between consecutive collisions are uniformly distributed in the interval $[19, 21]$. (b) corresponds to a strong coupling: collision times distributed in $[0.9, 1.1]$. The inset contains the same curves, after rescaling to the maximum values.

Apart from the residual statistical fluctuations, a reasonable agreement with expression (46) is found upon letting $\lambda = 0.056$ (approximately equal to the inverse of the average separation between consecutive collisions). Fig. 6b shows the results for the same length but a stronger coupling strength. The different shape of the curves is a clear indication that higher order terms must be taken into account, since the perturbative approach implies that the coupling constant acts just as a multiplicative factor. It is anyhow interesting that shape itself is invariant under change of δ as it can be seen in the inset where the three curves are rescaled to their maximum value.

Thermal conductivity - If obtaining an accurate analytic estimate of the flux is as difficult as determining the temperature profile, we can at least make use of eq. (40) to determine its scaling properties. In fact, since high-frequency eigenmodes are strongly localized, it is clear that only the first part of the spectrum contributes significantly to the flux. Let N_e be the number of modes whose localization length is larger than the sample size N. From eqs. (25,28), it follows that $\gamma \simeq \sigma_m^2 I(\omega)^2/\langle m \rangle$. Upon writing $I = N_e/N$ and imposing $\gamma = 1/N$, we find that

$$N_e = \frac{\langle m \rangle}{\sigma_m}\sqrt{N}. \tag{47}$$

At this point, it becomes crucial to specify the boundary conditions. Let us first consider the case of free ones: the square amplitude of an extended eigenmode in a lattice of size N is on the order $1/N$. This implies that the contribution to the flux of one of such modes is $\lambda(T_+ - T_-)/N$ and the total flux can be estimated as

$$J_{free}(\lambda, N) \propto \lambda(T_+ - T_-)\frac{\langle m \rangle}{\sigma_m}\frac{1}{\sqrt{N}}. \tag{48}$$

16

As a result the conductivity diverges as

$$\kappa_{free} \propto \lambda \frac{\langle m \rangle}{\sigma_m} \sqrt{N}. \tag{49}$$

This scaling was first derived in Ref. [22] and later confirmed in Ref. [24] by means of a different approach. On the other hand, for fixed boundary conditions the result is completely different. In this case all eigenmodes must vanish for $n = 0$ and $n = N + 1$. By approximating the site-to-site variation of e_n^k with the wavenumber k/N, we find that the square amplitude of e_1^k and e_N^k is on the order of k^2/N^3. As a consequence, summing all such addenda up to $k = N_e$ yields

$$J_{fix}(\lambda, N) \propto \lambda(T_+ - T_-) \left(\frac{\langle m \rangle}{\sigma_m} \right)^3 \frac{1}{N^{3/2}}. \tag{50}$$

and, accordingly, the thermal conductivity vanishes as

$$\kappa_{fix} \propto \lambda \left(\frac{\langle m \rangle}{\sigma_m} \right)^3 \frac{1}{\sqrt{N}}. \tag{51}$$

The above estimates give only the leading orders in N. In view of the previously encountered strong finite-size effects, it is crucial to check directly the convergence to the asymptotic results. To this aim it is convenient to compute the effective exponent

$$\alpha_{ef}(N) = \frac{d \ln \kappa}{d \ln N} \tag{52}$$

The results are shown in Fig. 7 for the case of fixed boundaries. For weak coupling, the conductivity has been evaluated by numerically computing the eigenvectors and averaging of Matsuda-Ishii formula (40) over 1000 realizations of the disorder. The asymptotic regime $\alpha = -1/2$ is approached very slowly (see the circles): one should consider N values much greater than 10^3. Similar results are found at stronger coupling by directly simulating chains that interact with stochastic baths. The data (diamonds in Fig. 7) suggest that a relatively strong coupling reduces the amplitude of finite-size corrections. Finally, it is important to realize that the small coupling of the exponentially localized modes with the thermal baths does not cause any problem to the temporal convergence of $J(\lambda, N)$, since independently of whether such modes have reached their stationary state, their contribution to the total flux is anyhow negligible.

In summary, not only boundary conditions affect the scaling behavior of κ, but they give rise to qualitatively different scenarios: for free boundaries, disordered harmonic chains exhibit an anomalous conductivity as it diverges in the thermodynamic limit. On the contrary, a disordered chain with fixed boundaries behaves as a good insulator ! This latter scenario is brought to an extremum if we add an on-site potential. In fact, we have already mentioned that all
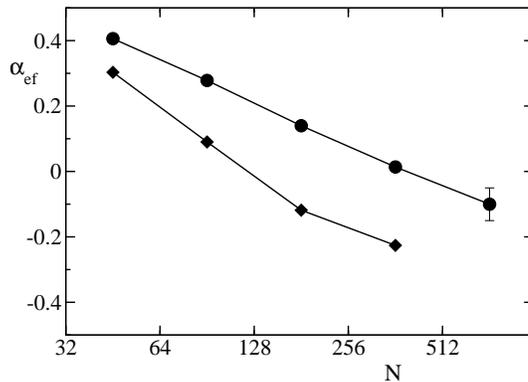
Fig. 7. The effective divergence exponent defined in (52) versus the chain length. The logarithmic derivative has been evaluated with finite differences, subsequent points correspond to chain of double length. Circles are obtained from the Matsuda-Ishii formula, while diamonds correspond to a direct simulation of a chain interacting with stochastic baths operating at $T_+ = 10$ and $T_- = 5$, respectively. The collision times were uniformly distributed in the range [1,2].

eigenfunctions become exponentially localized and this implies that conductivity is exponentially small in N. This is again very much reminiscent of the electrical conductivity of the Anderson's problem.

Let us conclude this section with a further comment on the role played by heat baths. Dhar [25] has shown how the scaling behavior of the conductivity with size depends also *on the spectral properties of the heat baths*. More precisely, if $\kappa \propto N^\alpha$ then the exponent α is determined by the low-frequency behavior of the noise spectrum. This implies that a suitable choice of the latter can even lead to a finite conductivity ! Such a scenario is less unphysical than it may appear at a first glance. Integrability of the motion implies that the only scattering mechanism that determine the heat resistance is the interaction with the baths. It is therefore reasonable that the actual way in which the latter transfer energy among the modes plays a crucial role.

4 The Boltzmann–Peierls approach to anharmonic disordered systems

In this section we briefly review the "traditional" approaches to the theory of thermal conductivity in anharmonic and disordered systems. Despite their major importance in solid state applications we will limit ourselves to a very sketchy discussion trying to point out some general issues that are of main interest for our purposes. In this respect, our presentation is inspired by the review article of Jackson [26].

The most elementary picture of heat conductivity is based on the analogy with the kinetic theory of gases where $\kappa = C v_s l / 3$, C is the heat capacity, v_s the sound velocity and l is the mean free path. For a lattice one has of course to take into account the different group velocities $v_{\mathbf{k}} = \frac{\partial \omega}{\partial \mathbf{k}}$ of normal modes. Upon introducing the relaxation times of each mode as $\tau_{\mathbf{k}} = l_{\mathbf{k}} / v_{\mathbf{k}}$

one obtains the formula

$$\kappa \;=\; \frac{1}{3}\int d\mathbf{k}\, C_{\mathbf{k}} v_{\mathbf{k}}^2 \tau_{\mathbf{k}} \quad . \tag{53}$$

In the spirit of Debye's model, dispersion is neglected and the above formula of kinetic theory is indeed recovered. A less heuristic derivation of such result can also be given by solving the Boltzmann equation in the relaxation time approximation [27]. The phenomenological relaxation times $\tau_{\mathbf{k}}$ account for all the possible scattering mechanisms (anharmonicity, impurities, scattering with the boundaries, electrons etc.) and must be computed in some independent way. The combined inverse phonon relaxation time is obtained as the sum of the inverse relaxation times corresponding to each process. Obviously, this approach relies crucially on the combined use of the concept of harmonic normal modes and on the adequacy of the relaxation time description.

In 1929 R. Peierls proposed his celebrated theoretical approach based on the Boltzmann equation. The main idea is again taken from the kinetic theory: lattice vibrations responsible for heat transport can be described as an interacting gas of phonons [2]. For simplicity, let us consider a one-dimensional ordered crystal and introduce the time-dependent distribution functions $N_k(x,t)$ of the phonons with wavenumber k in a small volume around the location x. Taking into account only the cubic term in the interaction potential (three-phonon processes), the kinetic equations are of the form

$$\frac{\partial N_k}{\partial t} + v_k \frac{\partial N_k}{\partial x} \;=\; \int\int dk' dk'' \{ [N_k N_{k'} N_{k''} - (N_k+1)(N_{k'}+1)N_{k''}]\, W_{kk'k''} \tag{54}$$

$$+ \frac{1}{2}\,[N_k(N_{k'}+1)(N_{k''}+1) - (N_k+1)N_{k'}N_{k''}]\, W_{kk'k''} \} \quad . \tag{55}$$

where the transition probability $W_{kk'k''}$ is basically obtained by the Fermi golden-rule. The r.h.s. is the collision integral i.e., the difference between the number of processes (per unit time) that increase or decrease the number of phonons in the state k. These nonlinear integro-differential equations are clearly impossible to solve in general [1].

Anyway, some useful informations about the heat conductivity can be obtained by analysing the dynamics in Fourier space of a system of anharmonic oscillators, where third and fourth order interaction terms are present(Fermi-Pasta-Ulam model):

$$\ddot{Q}_k \;=\; -\omega_k^2 Q_k - \sum_{k_1,k_2} V^{(3)}_{kk_1k_2} Q_{k_1} Q_{k_2} - \sum_{k_1,k_2,k_3} V^{(4)}_{kk_1k_2k_3} Q_{k_1} Q_{k_2} Q_{k_3} \quad . \tag{56}$$

---

[1] An approximate solution can be obtained in the limit of small applied gradients, i.e., by looking for small perturbation of the equilibrium distribution $N_k = N_k^{\mathrm{eq}} + \delta N_k$. This allows for the linearization of the collision integral [28,2]

Let us now consider the harmonic part of the flux

$$J_H = im \sum_k v_k \omega_k Q_k \dot{Q}_k^* \quad . \tag{57}$$

where we are considering a chain of N oscillators with equal mass m and

$$\omega_k = \frac{2}{\sqrt{m}} |sin(\frac{\pi \ k}{N})| \tag{58}$$

$v_k = \omega_k'$ is the phonon group velocity. Upon suitably rearranging the terms we can write the equation for its time derivative as

$$\dot{J}_H = \frac{im}{3} \sum_{kk_1k_2} [-v_k\omega_k + v_{k_1}\omega_{k_1} + v_{k_2}\omega_{k_2}] V^{(3)}_{-kk_1k_2} Q_k Q_{k_1} Q_{k_2} \tag{59}$$

$$+ \frac{im}{4} \sum_{kk_1k_2k_3} [-v_k\omega_k + v_{k_1}\omega_{k_1} + v_{k_2}\omega_{k_2} + v_{k_3}\omega_{k_3}] V^{(4)}_{-kk_1k_2k_3} Q_k Q_{k_1} Q_{k_2} Q_{k_3} \tag{60}$$

where the summations are over all k-indices. As expected, this implies that J_H is a constant of motion in the harmonic case. In a perfect lattice one has the selection rules (remember that the mode index k ranges between $-N/2+1$ and $N/2$):

$$V^{(3)}_{kk_1k_2} \neq 0 \qquad \text{for} \qquad -k + k_1 + k_2 = 0, \pm N \tag{61}$$

$$V^{(4)}_{kk_1k_2k_3} \neq 0 \qquad \text{for} \qquad -k + k_1 + k_2 + k_3 = 0, \pm N \tag{62}$$

Peierls observed that if there is no dispersion, i.e., $\omega_k = v_s|k|$, then both the three and four phonon contributions to (60) vanish if the sums in (62) are equal to zero. Therefore, the only contribution are those of the so-called *Umklapp* processes for which the sum is $\pm N$. The latter are the relevant ones in producing thermal resistance ($\dot{J}_H \neq 0$).

Besides the above general considerations, there are some important consequences regarding the role of dimensionality that can be drawn in the framework of the perturbative theories. Indeed, by evaluating the r.h.s of (60) to lowest order (i.e., by replacing the Q_k's with the harmonic solution $A_k e^{i\omega_k t}$) and performing an average over fast oscillations one is left with the leading resonant terms, that satisfy the additional conditions

$$\omega_k + \omega_{k_1} + \omega_{k_2} = 0 \qquad \omega_k + \omega_{k_1} + \omega_{k_2} + \omega_{k_3} = 0 \tag{63}$$

Thus there is a big difference among the three and four phonon processes in one dimension as in the former case the first of conditions (62) and (63) cannot be satisfied (see Ref.[29] for some numerical results). The net results of this argument due to Peierls is to conclude that there is only resistance to conduction in one dimension due to four phonon *Umklapp* processes.

Of course, in higher dimension the situation is different because the two constraints can be satisfied also for three phonon processes due to the existence of different (longitudinal and transverse) branches of the frequency spectrum. Notice also that, in the spirit of a perturbative calculation, only the harmonic component of the flux J_H has been considered, but the results are not basically altered when including also its nonlinear component [26].

Similar conclusion can be drawn from the analysis of the high-temperature limit of the Boltzmann equation following a standard argument originally due to Pomeranchuk (see for example Chapter VII in ref. [28]). Let us consider the effect of processes involving three long-wavelength phonons with wavenumbers k, k', k''. One can thus ascertain that in this limit the transition probability $W_{kk'k''} \sim kk'k'' \sim k^3$ and that $N_k^{\text{eq}} \sim 1/k$, thus implying that the solution of the linearized Boltzmann equation diverges as $\delta N_k \sim k^{-(2+d)}$ in dimension d. Using the corresponding expression for the heat flux yields

$$J_H \; \propto \; \int d\mathbf{k}\, \omega_\mathbf{k} v_\mathbf{k} \delta N_k \; \propto \; \int \frac{dk}{k^2} \tag{64}$$

Therefore, the contribution of such processes would lead to a thermal conductivity diverging like $1/k$ in any dimension. In order to avoid this divergence it is therefore necessary that long wavelength phonons are scattered by short-wavelength ones. A simple reasoning [28] shows that (in the absence of degeneration points in the spectrum) this is only possible if the group velocity of short wavelength phonons is *larger* than the sound velocity i.e., $|v_\mathbf{k}| > v_s$. Once again this constraint cannot be satisfied in one-dimensional homogeneous chains and one would conclude that a finite conductivity can be established only by means of higher order processes.

The Boltzmann-Peierls approach is certainly one of the milestones of the understanding of thermal transport in solids. Nonetheless, it is important to recall that its derivation is essentially based on second-order perturbation theory (through the collision kernel $W_{kk'k''}$, which is evaluated by means of Fermi's golden rule) and involves the use of random phase approximation among the phonon modes, which is certainly less appealing than the *Stosszahlansatz* originally introduced by Boltzmann for molecular collisions. It is however remarkable how classical perturbative approaches already indicate that some peculiarities have to be expected for anharmonic lattices in lower dimensions.

5   Linear response and transport coefficients

The other major approach which is commonly used when dealing with transport processes is linear response theory. At variance with the response to mechanical perturbations (e.g., an external electric field) the heat conduction process is due to boundary forces. Therefore, a conceptual difficulty arise as there is actually no small term in the system Hamiltonian that can be used as an expansion parameter. This difficulty can be overcome at the price of a stronger assumption, namely that *local equilibrium holds*. The hypothesis looks physically reasonable, but it is far from being rigorously based even in simple mathematical models and

it has been often devised as one of the weak points in the foundation of the whole theory. If local equilibrium holds, a temperature field $T(\mathbf{x})$ can be defined accordingly, thus allowing to introduce a nonequilibrium density matrix

$$\rho = Z^{-1} \exp\left(-\int d\mathbf{x}\beta(\mathbf{x})h(\mathbf{x})\right) \tag{65}$$

where $h(\mathbf{x})$ is the Hamiltonian density operator. If we assume $\beta(\mathbf{x}) = \beta(1 - \Delta T(\mathbf{x})/T)$ and that the deviations from global equilibrium are small the density matrix can be rewritten as

$$\rho = Z^{-1} \exp\left(-\beta(H + H')\right) \tag{66}$$

which defines a perturbation Hamiltonian

$$H' = -\frac{1}{T}\int d\mathbf{x}\Delta T(\mathbf{x})h(\mathbf{x}) \tag{67}$$

It is therefore possible to proceed with the perturbative expansion and to obtain the well known formula [30] ,that in the classical case reads

$$\kappa_{GK} = \frac{1}{k_B T^2}\lim_{t\to\infty}\int_0^t d\tau \lim_{V\to\infty} V\langle \mathbf{j}(\tau)\mathbf{j}(0)\rangle \tag{68}$$

where $\mathbf{j}$ is the volume-averaged heat flux defined in eq.(69). As often stated, the formula relates the nonequilibrium transport coefficient to the fluctuations of a system in equilibrium. A crucial issue, especially when dealing with simulations of a finite system, is that the infinite-volume limit should be taken before the long-time limit, in order to avoid the problem of Poincare' recurrences. Furthermore, this is a particularly delicate matter whenever a slow decay of correlations is present.

There is a basic and subtle issue regarding the application of the formula, that caused some confusion in the literature [31]. In the derivation *à la* Kubo sketched above $\langle\cdots\rangle$ denotes a canonical average. As it is well known, a formally identical expression was obtained by Green in the microcanonical ensemble, i.e., for an isolated system where energy is conserved. If also the total momentum P is conserved, it has to be set equal to zero otherwise $\langle \mathbf{j}\rangle \neq 0$ and the integral in eq.(68) would diverge [2]. Now, as already pointed out by Green himself [32], the microscopic expression of the heat flux, that has to be employed in the formula (68), *depends on the chosen ensemble*. Indeed, he showed that, in general, the expression

$$\mathbf{j} = \frac{1}{V}\sum_i \dot{\mathbf{x}}_i h_i + \frac{1}{2V}\sum_{j\neq i}(\mathbf{x}_i - \mathbf{x}_j)\mathbf{F}_{ij}(\dot{\mathbf{x}}_i + \dot{\mathbf{x}}_j) \tag{69}$$

---

[2] As observed in [3], one may alternatively use in eq.(68) the truncated correlation functions $\langle \mathbf{j}(t)\mathbf{j}(0)\rangle^T = \langle \mathbf{j}(t)\mathbf{j}(0)\rangle - \langle \mathbf{j}\rangle^2$ evaluated for $P \neq 0$.

is the correct one in the microcanonical case while a "counterterm" must be added to it in the canonical (or grand-canonical) one

$$\mathbf{j}_{can} = \mathbf{j}_{mic} - ev - Av - mv^2 v \qquad (70)$$

being v the velocity of the center of mass and A the pressure tensor. Up to terms of order $1/\sqrt{N}$

$$\mathbf{j}_{can} \simeq \mathbf{j}_{mic} - hv \qquad (71)$$

where h here denotes the specific enthalpy. Obviously, the two ensembles are expected to give the same result, provided that microcanonical energy density is chosen to correspond to the canonical temperature T. The reason why the same value of the transport coefficient is obtained using different expressions of the flux is that time-correlations of fluctuations can be different in different ensembles.

6 Mode–coupling theory and anomalous transport in low-dimensions

Despite the conceptual difficulties of the assumptions made for its derivation, eq. (68) provides a well defined prescription for obtaining thermal conductivity in terms of equilibrium quantities.

In particular, it implies that any knowledge about κ_{GK} can be traced back to a reliable estimate of the current-current correlation function. Making reference to the previous section we assume that our model of a solid – a regular lattice of coupled oscillators – is an isolated system described by the microcanonical ensemble, so that the current is given by the heat-flux vector in d space dimensions defined in (69) [3] .

An effective method for estimating the current-current correlation function can be obtained by applying the well known mode-coupling theory (MCT), introduced some decades ago for approaching the problem of long-time tails in fluids [4]. Since a rigorous proof of such a statement is lacking, we prefer to illustrate first some simple arguments that support this claim. Afterwards, we are going to draw the main quantitative consequences by applying MCT. Finally, we discuss in more technical detail the reliability of the above mentioned hypotheses, making reference to the 1D FPU model of coupled oscillators with cubic and quartic nonlinearities.

As we have mentioned in the previous section, the classical perturbative approach, that extends Peierls' one to the high temperature regime, already indicates that anomalous transport

---

[3] Thermal conductivity should be represented in general as a tensor. Here we assume to consider the simple case of an isotropic homogeneous solid made of atoms displaced on a regular hypercubic lattice, in the absence of any external force field. Accordingly, the thermal conductivity tensor has a diagonal representation, where each component reduces to the same scalar quantity. Upon this assumptions, κ_{GK} reduces to the scalar quantity defined in (68).

coefficients in low dimensional lattices should be expected. In fact, at high temperatures the non–linear components of the interaction play a major role and the behavior of hydrodynamic modes is expected to depend crucially on the mechanism of energy exchange among modes. At a first approximation, we can say that each mode k is characterized by a typical relaxation time scale proportional to the inverse of the damping factor γ_k. In models of fluids, γ_k vanishes continuously in the limit $k \to 0$. In this sense, it still plays the role of a perturbative parameter, implying that the damping effects are less and less relevant for hydrodynamic modes. Numerical studies performed for several models of anharmonic crystals with confining nearest-neighbor interactions, like the FPU or the Lennard-Jones models, exhibit the same scenario [33–35] in the high energy regime. Moreover, they also indicate that high-k modes behave like "thermal" variables, whose relaxation time scale is much faster [4]. Relying upon these observations, we are led to guess that Fourier modes in the above mentioned class of models can be represented at high energies as a fluid of quasi-particles, rather than a gas of weakly interacting phonons.

On the other hand, the effective value to be attributed to γ_k must be "renormalized" by taking explicitly into account that, due to the nonlinear nature of the interaction, all modes contribute, with different weights, to determine the hydrodynamic time scales. By exploiting the similarity with models of real fluids, we can expect that MCT [4,36] provides us the right tool for estimating the effective relaxation time scales of hydrodynamic modes. In particular, MCT predicts that the long-time behavior of any current-current correlation function in a fluid depends on how the effective damping factor $\gamma_k \to 0$ in the limit $k \to 0$. Accordingly, if the effective damping factor γ_k vanishes too rapidly for $k \to 0$ the time dependence of the heat-flux correlation function may be such that integral (68) diverges. In general this effect must depend also on the space dimension. Almost conserved modes propagating with sound velocity through the lattice are expected to propagate more efficiently in lower than in higher dimensions, where the presence of transverse modes favors the collision mechanism. Actually, a well defined, i.e., finite, transport coefficient in a model of anharmonic solid should emerge from an efficient dissipation mechanism eliminating all contributions associated with the ballistic propagation of sound waves. It is worth recalling that Fourier law is a consequence of the assumption that the temperature field obeys a diffusive equation.

Before entering any explicit treatment of MCT we want to summarize the main consequences of this approximate renormalization approach. According to MCT the leading contribution to the time dependence of the correlation function introduced in (68) is determined by the hydrodynamic propagator

$$\Gamma(k,t) \simeq \exp -\omega(k)t \tag{72}$$

----

[4] In the high–energy regime the mentioned models are known to exhibit strong chaotic properties, yielding an effective ergodicity. The separation of time scales between low-k and high-k modes seems to contradict this statement. This can be explained by observing that the low-k modes, playing a major role in transport effects, are a negligible fraction of the spectrum in the thermodynamic limit. Accordingly, for high energies equilibrium properties are dominated by thermal modes, while "hydrodynamic" deviations from ergodicity might be recovered in any finite system as higher order corrections to equilibrium averages.

where k is the modulus of the wave-vector $\mathbf{k}$, specifying the momentum coordinates in the Fourier space, dual to the lattice space coordinates. Specifically, one has

$$\langle \mathbf{j}(t)\mathbf{j}(0)\rangle \propto A(E) \int_0^\pi dk\, k^{d-1} \Gamma(k,t) \tag{73}$$

where $A(E)$ is a proportionality constant depending on the total energy E. The crucial point is that MCT predicts non-analytic dispersion relations for the complex quantity $\omega(k)$ [36], yielding the following asymptotic expansions at small values of k:

$$\omega(k) \simeq ick + \nu k^\alpha + \dots \qquad (d=1) \tag{74}$$
$$\omega(k) \simeq ick + \nu k^2 \ln k + \dots \qquad (d=2) \tag{75}$$
$$\omega(k) \simeq ick + \nu k^2 + \dots \qquad (d=3) \tag{76}$$

where c is the velocity of sound and the leading term of the relaxation rate $\gamma(k)$ is represented by the leading term of the low-k asymptotic expansion times a proper positive constant ν. **Notice that the results obtained for $d=2$ and for $d=3$ are model independent, while, as we shall see in the following, the exponent $\alpha > 1$, obtained for $d=1$, depends on the symmetry of the leading nonlinearity of the model.** Dimensional analysis yields the following dependence of the heat–flux correlation function at large time:

$$\langle \mathbf{j}(t)\mathbf{j}(0)\rangle \sim t^{-1/\alpha} \qquad (d=1) \tag{77}$$
$$\langle \mathbf{j}(t)\mathbf{j}(0)\rangle \sim t^{-1} \qquad (d=2) \tag{78}$$
$$\langle \mathbf{j}(t)\mathbf{j}(0)\rangle \sim t^{-3/2} \qquad (d=3) \tag{79}$$

Making reference to the definition of thermal conductivity (68), one can obtain the estimate of the dependence of κ on N from the asymptotic behavior of $\langle \mathbf{j}(t)\mathbf{j}(0)\rangle$, by considering that sound waves propagate with finite velocity c [5]. By restricting the integral in eq. (68) up to times smaller than the typical transit time N/c, the long time dependence can be translated into the large N dependence of κ:

$$\kappa \sim N^{(\alpha-1)/\alpha} \qquad (d=1) \tag{80}$$
$$\kappa \sim \ln N \qquad (d=2) \tag{81}$$
$$\kappa \sim finite \qquad (d=3) \tag{82}$$

---

[5] The case of rotators in $d=1$ represents a remarkable exception to anomalous heat conduction. Actually, despite conservation of energy and momentum still hold, the hydrodynamic equations do not yield any divergence because in this model there are no propagating sound waves. This can be easily guessed from the observation that the periodic potential of this model does not allow the existence of an acoustic band, as it happens for a confining nearest-neighbor interaction potential with a unique equilibrium position (minimum).

It is worth mentioning that numerical estimates of the size dependence of the heat conductivity κ in equilibrium and non-equilibrium simulations agree quite well with these quantitative predictions. Simulations confirm also the basic assumption of MCT, i.e. the separation of relaxation time scales between hydrodynamic (low-k) and thermal (high-k) Fourier modes.

For the sake of space we shall not go through the explicit derivation for the cases $d = 2$ and $d = 3$. The reader can find details in the references mentioned throughout this section. Anyway, these cases are much simpler to be derived than the case $d = 1$, which will be discussed in the following section.

7   MCT for chains with cubic and quartic nonlinearities

Here we illustrate how one can compute the relaxation times for the FPU model with cubic and quartic nonlinearities. We have already introduced in formula (56) the equations of motion of the 1d FPU model for the Fourier transformed coordinates

$$Q_k = N^{-1/2} \sum_{l=1}^{N} q_l \exp[-i(2\pi k/N)l] \tag{83}$$

where q_l are the lattice space coordinates, labelled by the integer index l, and $\omega_k = 2|sin(\pi k/N)|$, with the wave-number k ranging in the interval $[-N/2, N/2]$, are the usual harmonic frequencies of normal modes on a 1d lattice.

The pure cubic FPU-model ($V^{(4)} = 0$) should be studied in the MCT approach under the assumption that the nonlinear potential is a perturbation of the harmonic chain. In fact the lower unboundedness of the potential yields run-away solutions in the equations of motion for large nonlinearities. The addition of the quartic nonlinearity avoids this problem. On the other hand the hydrodynamic treatment of the cubic model is essentially dependent on the leading (cubic) nonlineariry and MCT calculations can be performed neglecting the contribution of the subleading (quartic) nonlinearity. As we shall see a different situation is obtained when the leading nonlinearity is quartic ($V^{(3)} = 0$). The symmetry of the even potential changes the very structure of the MCT and predicts a different value of the exponent α with respect to the cubic case.

Linear response theory provides a general method for representing the dynamics of slow variables, associated with the total momentum conservation law, in terms of suitable stochastic equations. Such slow variables are naturally represented by long-wavelength Fourier modes ($k << N$), that are assumed to behave almost uncorrelated from each other. Making reference to the standard formalism introduced by Kubo [30], one can introduce a projection operator $\mathcal{P}$ in phase space, acting on each scalar observable O as follows:

$$\mathcal{P}O = \sum_k \left[\frac{\langle OQ_k^* \rangle}{\langle |Q_k|^2 \rangle} Q_k + \frac{\langle OP_k^* \rangle}{\langle |P_k|^2 \rangle} P_k \right] \tag{84}$$

where the average $\langle\cdots\rangle$ is assumed over the time scale of fast variables and $P_k = \dot{Q}_k$ is the momentum coordinate (for unit mass particles), canonically conjugated with Q_k. The projected equations of motion then read

$$\ddot{Q}_k = -\tilde{\omega}_k^2 Q_k - \int_0^t \Gamma_k(t-s)P_k(s)ds + R_k \tag{85}$$

where the random force $R_k = (1 - \mathcal{P})\ddot{Q}_k$ is related to the memory kernel $\Gamma_k(t-s)$ by the fluctuation-dissipation theorem:

$$\Gamma_k(t) = \beta\langle R_k(t)R_k^*(0)\rangle \tag{86}$$

where β is the inverse reduced temperature of thermal modes at equilibrium. Nonlinear effects are partially included into the renormalized frequency

$$\tilde{\omega}_k^2 = (\beta\langle|Q_k|^2\rangle)^{-1} = (1+\alpha)\omega_k^2 \quad , \quad \alpha(\beta) = \frac{1}{\beta}\frac{\int \exp -\beta V(x)dx}{\int x^2 \exp -\beta V(x)dx} - 1 \tag{87}$$

that, in practice, amounts to a renormalization of the "harmonic" velocity of sound c to a temperature dependent value $\tilde{c} = c\sqrt{1+\alpha}$. A straightforward consequence of eq. (85) is that the normalized correlation function

$$G_k(t) = \beta\tilde{\omega}_k^2\langle Q_k(t)Q_k(0)\rangle \tag{88}$$

obeys the equation of motion

$$\ddot{G}_k(t) + \tilde{\omega}_k^2 G_k(t) = -\int_0^t \Gamma_k(t-s)\dot{G}_k(s)ds \quad . \tag{89}$$

By passing to the Laplace transforms of $G_k(z)$ and $\Gamma_k(z)$ with the definition

$$A_k(z) = \int_0^\infty e^{-izt}A_k(t)dt \tag{90}$$

equation (89) yields the relation:

$$G_k(z) = \frac{iz + \Gamma_k(z)}{z^2 - \tilde{\omega}_k^2 - iz\Gamma_k(z)} \tag{91}$$

Up to here we have illustrated some formal manipulation of the equations of motion along the strategy of linear response theory [30]. The crucial conceptual point is the explicit computation

of the memory kernel $\Gamma_k(t)$. MCT is an approximate self-consistent method for obtaining such an expression in terms of $G_k(t)$. The first step of this procedure amounts to the replacement

$$\langle R_k(t)R_k^*(0)\rangle \rightarrow \langle \mathcal{F}_k(t)\mathcal{F}_k^*(0)\rangle \tag{92}$$

where $\langle \cdots \rangle$ represents the equilibrium average and $\mathcal{F}_k(t)$ is a shorthand notation for the **non-linear component of the forces**, i.e., the last two addenda on the r.h.s. of eq. (56). Actually $R_k(t)$ cannot be explicitly determined, since it does not obey standard Liouvillean evolution. The above replacement implies also that slow terms possibly contained in $\mathcal{F}_k(t)$ (and absent in $R_k(t)$) can be neglected in the thermodynamic limit. On the basis of plausibility considerations (see [4,37]) it can be argued that the leading contribution to the correlator on the r.h.s. of eq. (92) is given by the resonating terms, obeying the conditions $k_1 = -k_2$ and $k_1 - k_2 - k_3 = 0$ (see eq.(60)) for the cubic and quartic components, respectively.

For the cubic term this approximation yields the relation

$$\Gamma_k(t) = \beta\langle\mathcal{F}_k(t)\mathcal{F}_k^*(0)\rangle \approx C(\beta)\omega_k^2\frac{1}{N}\sum_{k'}G_{k'}(t)G_{k-k'}(t) \tag{93}$$

where $C(\beta) = \frac{3}{\beta(1+\alpha)^2}\,(g_3^2)$, where g_3 is the cubic coupling constant.

Performing the thermodynamic limit, $N \rightarrow \infty$ and passing to the continuous variable representation $2\pi k/N \rightarrow q$, the sum in eq. (93) can be replaced by an integral:

$$\Gamma(q,t) = \epsilon\omega(q)^2\int_{-\pi}^{\pi}\mathrm{d}pG(p,t)G(q-p,t) \tag{94}$$

where $epsilon = \frac{3g_3^2 K_B T}{2\pi}$ and $\omega(q)$ obeys the bare dispersion relation (with the sound velocity $c = 1$):

$$\omega(q) = 2\,|sin\frac{q}{2}| \tag{95}$$

When the leading nonlinearity is the quartic one the last equation changes to

$$\Gamma(q,t) = \epsilon\omega(q)^2\int_{-\pi}^{\pi}\mathrm{d}p\int_{-\pi}^{\pi}\mathrm{d}nG(p,t)G(n,t)G(q-p-n,t) \tag{96}$$

In Appendix 2 we report the procedure for solving the cubic case. For the sake of space the solution of the quartic case is omitted, although the reader can try to obtain it by repeating (with a few more technical difficulties) the same kind of calculations.

Here we just mention the main results: for the cubic case $\alpha = 3/2$ and in the quartic case $\alpha = 2$. This implies that the heat conductivity κ in chain of nearest-neighbor coupled nonlinear oscillators exhibits different power-law divergence in the thermodynamic limit when the leading nonlinearity is cubic or quartic, namely

$$\kappa \sim N^{1/3} \qquad cubic \ \ case \tag{97}$$
$$\kappa \sim N^{1/2} \qquad quartic \ \ case \tag{98}$$

Let us point out that recent numerical simulations [38] agree quite well with these MCT predictions. On the other hand one should consider that quartic case is quite a peculiar situation. In fact, by adding pressure at the chain ends, after having introduced a lattice length scale (which is completely absent in the FPU models) one can easily argue that the quartic problem can be reformulated as an effective cubic case. In this perspective the power-law divergence of the quartic FPU model seems quite an exception of the 1/3 divergence. In real materials, where exact one-dimensional structure are quite difficult to be designed, one expects to recover power law divergences typically smaller than but close to the value 1/3.

Acknowledgments

APPENDIX 1: Solution of the Harmonic Homogeneous Chain

In this Appendix, we present a procedure very close to that adopted in Ref. [17] for solving the Fokker-Planck equation (3) for a homogeneous harmonic chain. Starting from the equilibrium solution (12), let us define

$$
\begin{aligned}
\overline{\mathbf{U}} &\equiv \mathbf{U}_e + \frac{k_B(T_+ - T_-)}{2\omega^2}\mathbf{U} \\
\overline{\mathbf{V}} &\equiv \mathbf{V}_e + \frac{k_B(T_+ - T_-)}{2}\mathbf{V} \\
\overline{\mathbf{Z}} &\equiv \frac{k_B(T_+ - T_-)}{2\lambda}\mathbf{Z} \quad,
\end{aligned}
\tag{99}
$$

From eq. (9), it follows that $\mathbf{U}$, $\mathbf{V}$ and $\mathbf{Z}$ satisfy the equations,

$$\mathbf{Z} = -\mathbf{Z}^\dagger \tag{100}$$
$$\mathbf{V} = \mathbf{U}\mathbf{G} + \mathbf{Z}\mathbf{R} \tag{101}$$

$$2\mathbf{S} - \mathbf{VR} - \mathbf{RV} = \nu[\mathbf{GZ} - \mathbf{ZG}] \tag{102}$$

where $\nu = \omega^2/\lambda^2$ is the only, dimensionless, parameter that matters. In addition, $\mathbf{U}$ and $\mathbf{V}$ are required to be symmetric. From the peculiar structure of the matrices $\mathbf{R}$ and $\mathbf{S}$, it follows that the l.h.s. of eq. (102) is a *bordered* matrix (i.e., its only nonvanishing elements are located on the external columns and rows). Accordingly, the r.h.s. must be bordered as well, i.e., in the bulk, $\mathbf{Z}$ commutes with G. The most general structure of a matrix commuting with $\mathbf{G}$ in the interior is the linear combination of a matrix M_{ij}^d with equal elements along the diagonals ($i+j$ constant) and a matrix M_{ij}^c with equal elements along the cross-diagonals ($i-j$ constant). The antisymmetry requirement for $\mathbf{Z}$ (see eq. (100)), implies that no contribution of the second type is present and, more precisely, that

$$Z_{ij} = \phi(j - i) \tag{103}$$

with the further constraint $\phi(j) = -\phi(-j)$. The quantities $\phi(j)$ are fixed by equating the border elements of the commutator $[G, Z]$ (multiplied by ν) with those of the l.h.s. of eq. (102),

$$\nu\phi(j) = \delta_{j1} - V_{1j} = \delta_{j1} + V_{N,N-j+1} \tag{104}$$

where $\phi_N \equiv 0$ by definition. From eq. (101) and its transposed expression it follows that $\mathbf{U}$ satisfies a similar relation to that for Z,

$$\mathbf{GU} - \mathbf{UG} = \mathbf{RZ} + \mathbf{ZR}. \tag{105}$$

Accordingly, also $\mathbf{U}$ commutes with G in the bulk. The different symmetry property of $\mathbf{U}$ with respect to $\mathbf{Z}$ implies, however, that $\mathbf{U}$ is constant along the cross-diagonals. It is easy to verify that a solution of eq. (105) is given by

$$U_{ij} = \begin{cases} \phi(i + j - 1) & \text{if } i + j \leq N \\ \phi(2N + 1 - i - j) & \text{if } i + j \geq N \end{cases}. \tag{106}$$

In principle, this is not the only solution of eq. (105), as one can add any symmetric matrix commuting with G; however, one can check a posteriori that the addition of any such matrix would eventually violate the symmetry properties of $\mathbf{V}$.

As a result of eq. (106), also the matrix $\mathbf{X}$ can be expressed in terms of the auxiliary variables $\phi(j)$. By replacing the $\mathbf{Z}$ and $\mathbf{X}$ solutions in the r.h.s. of eq. (101), we both obtain an equation for the vector $\phi(j)$,

$$\sum_{j=1}^{N-1} K_{ij}\phi(j) = \delta_{1i}, \tag{107}$$

30

where $\mathbf{K} = \mathbf{G} + \nu\mathbf{I}$, and the following expression for $\mathbf{V}$,

$$\mathbf{V} = \mathbf{S} - \nu\mathbf{U}. \tag{108}$$

The problem of finding a solution for the heat transport in a homogeneous chain is accordingly reduced to solving eq. (107) that can be written as the recursive relation

$$\phi(j+1) = (\nu+2)\phi(j) - \phi(j-1) \tag{109}$$

which has to be complemented by suitable initial and final conditions. From the above equation, it follows that $\phi(j)$ is the linear combination of two exponentials $\exp(\pm\alpha j)$ with

$$e^{-\alpha} = 1 + \frac{\nu}{2} - \sqrt{\nu + \frac{\nu^2}{4}} \tag{110}$$

Upon imposing the appropriate initial conditions, we finally obtain

$$\phi(j) = \frac{\sinh(N-j)\alpha}{\sinh N\alpha} \tag{111}$$

which completes the solution for the stationary probability distribution.

APPENDIX 2: Mode-coupling approach to low-dimensional transport

The mode-coupling equations for the cubic FPU model, in dimensionless units of mass, lattice spacing and bare sound velicity($m = a = c = 1$) read

$$\ddot{G}(q,t) + \int_0^t \Gamma(q,t-s)\dot{G}(q,s)\,ds + \omega^2(q)G(q,t) \;=\; 0 \tag{112}$$

$$\Gamma(q,t) = \epsilon\,\omega^2(q)\int_{-\pi}^{\pi} dp\,G(p,t)G(q-p,t) \tag{113}$$

where

$$\epsilon = \frac{3g_3^2 K_B T}{2\pi} \tag{114}$$

$$\omega(q) = 2|sin\frac{q}{2}| \tag{115}$$

Notice that in the thermodynamic limit (113) represent an infinite set of equations, depending on the wavenuber q.

This set of equations is derived by assuming that the main contribution to the hydrodynamic behavior comes from the coupling among *sound modes* (associated with the conservation of density and momentum and characterized by a ballistic propagators). The coupling with *heat modes* (associated with energy conservation and diffusive propagators) is assumed to be so weak to be neglected (this is exactly the case for a hard point gas). Numerical tests performed for the FPU models confirm the validity of this assumption.

We want to solve this set of self-consistent equations with the initial conditions $G(q,0) = 1$ and $\dot{G}(q,0) = 0$.

The physical meaning of these equations can be understood as follows. Let us assume that a Markovian approximation holds i.e. we replace the memory function by a Dirac distribution

$$\int_{-\pi}^{\pi} dp\, G(p,t)G(q-p,t) \approx \delta(q-p) \tag{116}$$

The first equation of (113) for small values of q reduces to the form

$$\ddot{G}(q,t) + \eta q^2 \dot{G}(q,t) + c^2 q^2 G(q,t) = 0 \tag{117}$$

According to linear elasticity theory [39], this equation is equivalent to the one representing the evolution of a macroscopic displacement field $u(x,t)$ of an elastic string at at finite temperature:

$$\ddot{u} - \partial_x^2 u + \eta \partial_x^2 \dot{u} = 0 \quad . \tag{118}$$

where η is a suitable viscosity coefficient which takes into account the internal irreversible processes.

We would like to solve the set of self-consistent equations (113) with the initial conditions $G(q,0) = 1$ and $\dot{G}(q,0) = 0$. More precisely, we aim at computing explicitely the scaling properties of the correlation function $G(q,t)$, consistently with $\Gamma(q,t)$.

In order to apply a scaling argument like the one used in [40] for a Heisenberg spin chain at finite temperature we have first to reduce the second order PDE's to first order PDE's. Such a task can be accomplished by assuming that there are two different time scales (*multiscale analysis*): a slow one associated with the dissipation and a fast one associated with the oscillation of $G(q,t)$. Accordingly, we rewrite the first of (113) as follows:

$$\ddot{G}(q,t,\epsilon) + \int_0^t \Gamma(q,t-s,\epsilon)\dot{G}(q,s,\epsilon)\,ds + \omega^2(q)G(q,t,\epsilon) = 0 \tag{119}$$

We introduce the long time scale $\tau = \mu t$, with $\mu = \sqrt{\epsilon}$ and we consider t and $\tau = \mu t$ as independent time variables. The time-derivative and the time-integration operators transform as

$$\frac{d}{dt} \rightarrow \frac{\partial}{\partial t} + \mu \frac{\partial}{\partial \tau} \tag{120}$$

e

$$\int dt \rightarrow \frac{1}{\mu} \int dt \int d\tau \tag{121}$$

eq.(119) can be rewritten as follows:

$$\frac{\partial^2}{\partial t^2} G(q, t, \tau) + 2\mu \frac{\partial^2}{\partial t \partial \tau} G(q, t, \tau) + \mu^2 \frac{\partial^2}{\partial \tau^2} G(q, t, \tau)$$
$$+ \frac{1}{\mu} \int_0^t dt' \int_0^\tau d\tau' \Gamma(q, t - t', \tau - \tau') \left(\frac{\partial}{\partial t} G(q, t', \tau') + \mu \frac{\partial}{\partial \tau} G(q, t', \tau') \right) + \omega^2 G(q, t, \tau) = 0 \tag{122}$$

Consistently with the multiscale aproach we assume that also $G(q, t)$ can be expressed by the perturbative expansion:

$$G(q, t, \tau) = G_0(q, t, \tau) + \mu \, G_1(q, t, \tau) + O(\mu^2) \tag{123}$$

This means that the decay time-scale associated with dissipation is ruled by the perturbative parameter μ, in such a way that $\tau \ll t$. The zero-order equation obtained from (122) reads:

$$\frac{\partial^2}{\partial t^2} G_0(q, t, \tau) + \omega(q)^2 G_0(q, t, \tau) = 0 \tag{124}$$

which yields the straightforward solution:

$$G_0(q, t, \tau) = C(q, \tau) e^{i\omega(q)t} + c.c. \tag{125}$$

The amplitude $C(q, \tau)$ can be determined by solving the equation obtained from (122) at the first order expansion in μ:

$$-2\mu \frac{\partial}{\partial \tau} \left(i\omega(q) C(q, \tau) e^{i\omega(q)t} + c.c. \right) - \frac{1}{\mu} \int_0^t dt' \int_0^\tau d\tau' \Gamma(q, t - t', \tau - \tau') \left(i\omega(q) C(q, \tau') e^{i\omega(q)t'} + c.c. \right)$$
$$= \mu \frac{\partial^2}{\partial t^2} G_1(q, t, \tau) + \mu \omega(q)^2 G_1(q, t, \tau) \tag{126}$$

where $G_0(q, t, \tau)$ has been replaced by its explicit solution (125). Now we consider the memory function, which has the general form:

$$\Gamma(q, t, \tau) = \mu^2 \int\limits_0^{+\infty} d\Omega \left[M(q, \tau, \Omega) e^{i\Omega t} + c.c. \right] \qquad (127)$$

By substituting (127) into (126) the integral is found to contain exponentials of the form $e^{\pm i(\omega - \Omega)t}$ and $e^{\pm i(\omega + \Omega)t}$. According to time-dpendent perturbation theory the latter can be neglected, while the former yield the *resonance condition* $\Omega = \omega$. By imposing the Fredholm conditions (i.e. orthogonality w.r.t. $e^{\pm i\omega(q)t}$) on the r.h.s. of eq. (126) one obtains

$$2\frac{\partial}{\partial \tau} C(q, \tau) + \int\limits_0^\tau d\tau' M(q, \tau, \omega) C(q, \tau') = 0 \qquad (128)$$

and an equivalent equation for the complex conjugate $C^*(q, \tau)$. It remains to obtain an explicit expression for $M(q, \tau, \Omega)$. This can be obtained by recalling that in the cubic FPU model the memory function has the form

$$\Gamma(q, t) = \mu^2 \omega^2(q) \int\limits_{-\pi}^\pi dp\, G(p - q/2, t) G(p + q/2, t) \qquad (129)$$

By substituting the expression of $G(p, t)$ in (125) one obtains

$$\begin{aligned}
\Gamma(q, t, \tau) = \mu^2 q^2 \int\limits_{-\pi}^\pi dp [& C(p - q/2, \tau) C(p + q/2, \tau) e^{i\omega(p-q/2)t} e^{i\omega(p+q/2)t} \\
& + C(p - q/2, \tau) C^*(p + q/2, \tau) e^{i\omega(p-q/2)t} e^{-i\omega(p+q/2)t} \\
& + C^*(p - q/2, \tau) C(p + q/2, \tau) e^{-i\omega(p-q/2)t} e^{i\omega(p+q/2)t} \\
& + C^*(p - q/2, \tau) C^*(p + q/2, \tau) e^{-i\omega(p-q/2)t} e^{-i\omega(p+q/2)t}]
\end{aligned} \qquad (130)$$

Since we want to take into account the hydrodynamic limit ($q \to 0$) the previous expression simplifies to

$$\begin{aligned}
\Gamma(q, t, \tau) = \mu^2 q^2 \int\limits_{-\pi}^\pi dp [& C(p - q/2, \tau) C(p + q/2, \tau) e^{i2\omega(p)t} + C(p - q/2, \tau) C^*(p + q/2, \tau) e^{-i\omega'(p)qt} \\
& + C^*(p - q/2, \tau) C(p + q/2, \tau) e^{i\omega'(p)qt} + C^*(p - q/2, \tau) C^*(p + q/2, \tau) e^{-2i\omega(p)t}]
\end{aligned} \qquad (131)$$

where $\omega'(p) = \frac{d\omega}{dp} |_{q=0}$. The first and the fourth addenda are negligible, and if we assume that

34

the velocity of sound c is independent of q we obtain:

$$\Gamma(q,t,\tau) = \mu^2 q^2 \left[\int_{-\pi}^{\pi} dp C^*(p-q/2,\tau)C(p+q/2,\tau)e^{icqt} + \int_{-\pi}^{\pi} dp C(p-q/2,\tau)C^*(p+q/2,\tau)e^{-icqt} \right] \quad (132)$$

By comparing this expression with (127) one obtains

$$\Gamma(q,t,\tau) = \mu^2 M(q,\tau)e^{ic|q|t} + c.c. \quad (133)$$

Accordingly, $M(q,\tau)$ can be identified with $q^2 \int_{-\pi}^{\pi} dp C^*(p-q/2,\tau)C(p+q/2,\tau)$. At first order in the perturbative approach we obtain the new set of self-consistent equations

$$2\frac{\partial}{\partial\tau}C(q,\tau) + \int_0^{\tau} d\tau' M(q,\tau,\omega)C(q,\tau') = 0$$

$$M(q,\tau) = q^2 \int_{-\pi}^{\pi} dp C^*(p-q/2,\tau)C(p+q/2,\tau) \quad (134)$$

Notice that this set of equations are first-order PDE which describe the slow decay of the amplitude of correlation functions. Any dependence on the short time scale typical of fast oscillations has disappeared and, in practice, we are going to solve a sort of *envelope equations*. In particular, we aim at computing the scaling properties of both functions $C(q,\tau)$ and $M(q,\tau)$, by assuming that the following scaling relation holds

$$C(q,\tau) = C(q\lambda^a, \tau\lambda^b) \quad , M(q,\tau) = \lambda M(q\lambda^a, \tau\lambda^b)$$

Simple calculations yield $a = -1/3$ and $b = 1/2$. Accordingly, the solutions have the form:

$$C(q,\tau) = g(\tau q^{3/2}) \quad (135)$$
$$M(q,\tau) = q^3 f(\tau q^{3/2}) \quad (136)$$

The asymptotics of these solutions in the τ and q variables can be obtained without finding the explicit form of these solutions. We obtain

$$M(q,\tau) = q^2 \int dp\, g^2(\tau p^{3/2}) = \lambda^{4/3}\frac{q^2}{\tau^{2/3}} \quad (\tau \to \infty,\ q \to 0) \quad (137)$$

and finally

$$\Gamma(q,t,\tau) = \mu^2 \left[M(q,\tau)e^{icqt} + M^*(q,\tau)e^{-icqt} \right] \sim \mu^2 q^2 \frac{e^{icqt} + e^{-icqt}}{\tau^{2/3}} \quad (138)$$

By reintroducing the original time variable t we find:

$$\Gamma(q,t,\tau) = \mu^{\frac{4}{3}} q^2 \frac{e^{icqt} + e^{-icqt}}{t^{2/3}} \tag{139}$$

Notice that one can also obtain the explicit expression for the Laplace transform $C(q,z)$ of $C(q,t)$ by substituting (137) into the first of (134):

$$C(q,z) = \frac{i}{iz + \lambda^{4/3} q^2 z^{-1/3}} = \frac{iz^{1/3}}{iz^{4/3} + \lambda^{4/3} q^2} = \frac{iz^{1/3}}{iz^{4/3} + (\lambda q^{\frac{3}{2}})^{4/3}} \tag{140}$$

Here λ is a suitable constant.

It is worth pointing out that this is the Laplace transform of the Mittag-Leffler special function $E_\alpha(-(\tau\gamma)^\alpha)$. In our case $\alpha = 4/3$ e $\gamma = \lambda q^{3/2}$. The asymptotis of this function in the limits $\tau \to 0$ and $\tau \to \infty$ is given by :

$$exp[-(\lambda q^{3/2}\tau)^{4/3}], \quad \lambda q^{3/2}\tau << 1 (\lambda q^{3/2}\tau)^{4/3}, \quad \lambda q^{3/2}\tau >> 1 \tag{141}$$

Notice that both asymptotics determine the same scaling relation for the heat-flux correlation function.

Analogously, we can consider the Lapalace transform of (139), which has the form:

$$\Gamma(q,z) = \mu^{\frac{4}{3}} q^2 \left[(z - c \mid q \mid)^{-\frac{1}{3}} + (z + c \mid q \mid)^{-\frac{1}{3}} \right] \tag{142}$$

where

$$\Gamma(q,z) = \int_0^\infty e^{-izt} \Gamma(q,t) dt \tag{143}$$

By Lapalace-transforming the first of (113) one has the formal solution (with $\dot{G}(q,0) = 0$)

$$G(q,z) = \frac{iz + \Gamma(q,z)}{z^2 - \omega^2(q) - iz\Gamma(q,z)} \tag{144}$$

$$\Gamma(q,z) = M(q) \int dz' \int dp \, G(p, z - z') G(q - p, z') \tag{145}$$

where the integration on z' is along the real axis (inverted Laplace transform) and we have introduced $M(q) = \epsilon\omega^2(q)$. One can expect that the dissipative effects are weak for small values of q, so that the first of eq.s (145) can be approximated as follows

$$G(q,z) = G_-(q,z) + G_+(q,z) = \frac{-i/2}{z - \omega(q) - i\Gamma(q,z)/2} + \frac{-i/2}{z + \omega(q) - i\Gamma(q,z)/2} \tag{146}$$

36

Notice that by this approximation we have disregarded in the numerator terms like Γ/ω. They are expected to contribute as small phase factors, which can be neglected at least in the limit $q \to 0$. By substituting (142) into (146) we can compute the poles of the correlation function. They are located at:

$$\pm c \mid q \mid + i\sqrt{\epsilon} \mid q \mid^{\frac{3}{2}} \tag{147}$$

which indicates that the exponent $\alpha = 3/2$ in the cubic FPU model, so that the thermal conductivity diverges in the thermodynamic limit as

$$\kappa_3 \sim N^{1/3} \tag{148}$$

.

For what concerns the quartic FPU model ($g_3 = 0$, $g_4 \neq 0$) even more tedious calculations performed by the same multiscale analysis yield a much simpler expression for the Laplace transform of the amplitude of the correlation function

$$C(q, z) = \frac{i}{iz + \lambda q^2} \tag{149}$$

which yields a time decay of the heat-flux correlation function

$$\langle J(t)J(0) \rangle \approx \int \mathrm{d}q g^2(tq^2) \sim t^{-1/2} \tag{150}$$

Accordingly, this implies that the heat conductivity diverges in the thermodynamic limit as

$$\kappa_4 \sim N^{1/2} \tag{151}$$

References

[1]   de Groot S R and Mazur P, 1984 *Non–equilibrium Thermodynamics* Dover, New York.

[2]   Peierls R E, 1955 *Quantum theory of solids*, Oxford University Press, London.

[3]   Bonetto F, Lebowitz J L and Rey-Bellet K, 2000 in: A. Fokas, A. Grigoryan, T. Kibble and B. Zegarlinski (Eds.), *Mathematical Physics 2000*, Imperial College, London.

[4]   Pomeau Y and Résibois R, 1975 Phys. Rep. **19** 63.

[5]   Morelli D T, Heremans J, Sakamoto M and Uher C, 1986 Phys. Rev. Lett. **57** 869.

[6]   Smontara A, Lasjaunas J C and Maynard R, 1996 Phys. Rev. Lett. **77** 5397.

[7] Sologubenko A V et al., 2001 Phys. Rev. **B64** 054412.

[8] Forsman H and Anderson P, 1984 J. Chem. Phys. **80** 2804.

[9] Tighe T S, Worlock J M and Roukes M L, 1997 Appl. Phys. Lett. **70** 2687.

[10] Leivo M M and Pekola J P, 1998 Appl. Phys. Lett. **72** 1305.

[11] Holmes W et al. , 1998 Appl. Phys. Lett. **72** 2250.

[12] Hone J et al., 1999 Phys. Rev., **B59** R2514.

[13] Kim P, Shi L, Majumdar A and McEuen P L, 2001 preprint cond-mat/0106578.

[14] L.G.C. Rego L G C and Kirczenow G, 1998 Phys. Rev. Lett. **81** 232.

[15] D.M. Leitner DM and Wolynes P G, 2000 Phys. Rev. **E61** 2902.

[16] Rubin R J and Greer W L, 1971 J. Math. Phys. **12** 1686 .

[17] Rieder Z, Lebowitz J L and Lieb E, 1967 J. Math. Phys. **8** 1073.

[18] Wang M C and Uhlenbeck G E, 1945 Rev. Mod. Phys. **17**, 323.

[19] Bolsterli M, Rich M and Visscher W M, 1970 Phys. Rev. **A1** 1086.

[20] Casher A, Lebowitz J L, 1971 J. Math. Phys. **12** 1701 .

[21] O'Connor A J, Lebowitz J L, 1974 J. Math. Phys. **15** 692 .

[22] Matsuda H and Ishii K, 1970 Suppl. Prog. Theor. Phys. **45** 56.

[23] Visscher W M, 1971 Prog. Theor. Phys. **46** 729.

[24] Keller J B, Papanicolaou G C and Weilenmann J, 1978 Comm. Pure and App. Math. **Vol. XXXII** 583.

[25] Dhar A, 2001 Phys. Rev. Lett. **86** 5882.

[26] Jackson E A, 1978 Rocky Mount. J. Math. **8** 127.

[27] Callaway J, 1991 *Quantum theory of the solid state*, Academic Press, San Diego.

[28] Lifshitz E L and Pitaevskij L P, 1981 *Physical Kinetics*, Pergamon Press, New York.

[29] Lepri S, 2000 Eur. Phys. J. **B18** 441.

[30] Kubo R, Toda M and Hashitsume N, 1991 *Statistical Physics II*; Springer Series in Solid State Sciences, **Vol. 31** Springer, Berlin.

[31] Prosen T and Campbell D K, 2000 Phys. Rev. Lett. **84** 2857.

[32] Green M S, 1960 Phys. Rev. **119** 829.

[33] Alabiso C, Casartelli M and Marenzoni P, 1995 J. Stat. Phys. **79** 451.

[34] Lepri S, Livi R and Politi A, 1997 Phys. Rev. Lett. **78** 1896.

[35] Lepri S, Livi R and Politi A, 1998 Physica **D119** 140.

[36] Ernst M H, 1991 Physica **D47** 198.

[37] Lepri S, 1998 Phys. Rev. **E58** 7165.

[38] Delfini L, Lepri S, Livi R and Politi A, 2006 preprint ,submitted to Phys. Rev. **E**.

[39] Landau-Lifchitz "Elasticity theory" eq. (32.2).

[40] S. W. Lovesey, E. Balcar, J. Phys. Condens. Matter **6** (1994) 1253.