PHYSICAL REVIEW E **82**, 040101(R) (2010)

Graded anharmonic crystals as genuine thermal diodes: Analytical description of rectification and negative differential thermal resistance

Emmanuel Pereira*
Departamento de Física–ICEx, UFMG, CP 702, 30.161-970 Belo Horizonte, MG, Brazil

(Received 25 May 2010; published 1 October 2010)

We address the heat flow study starting from microscopic models of matter: we develop an approach and investigate some anharmonic graded mass crystals, with weak interparticle interactions. We calculate the thermal conductivity, and show the existence of rectification and negative differential thermal resistance. Our formalism allows us to understand the mechanism behind the phenomena, and shows that the properties of graded materials make them genuine thermal diodes.

DOI: 10.1103/PhysRevE.82.040101 PACS number(s): 05.70.Ln, 05.40.−a, 44.10.+i

Many works are devoted to the problem of understanding the heat flow starting from microscopic models of matter [1], and most of them are carried out by means of computer simulations, sometimes with inconclusive results. It creates a demand for analytical studies, but, since Debye, the microscopic models used to describe heat conduction are mainly given by systems of anharmonic oscillators, which involve problems without precise solutions. Anyway, interesting properties have been discovered and their use proposed: e.g., the possibility to control the heat flow by using nanodevices such as thermal diodes, transistors, memories, etc. [2–7]. The basic structure of these objects, the thermal diode, is a device in which heat flows preferably in one direction. There are analytical attempts to explain this phenomenon and/or design a diode by using simple methods [6,8,9], but, again, most of the works are carried out by means of computer simulations [2–4]. A recurrently used design of diodes is given by the sequential coupling of chains with different anharmonic potentials [2–4]. Although frequently investigated, it is criticized due to the difficulty to be constructed in practice [3]. Recently, Chang *et al.* [7] built a diode in a experimental work by using a different procedure: graded materials, i.e., nanotubes externally and inhomogeneously mass loaded with heavy molecules. Numerical computations [10] also indicate rectification in a graded anharmonic system with abnormal conductivity.

An important effect noticed in these studies is the negative differential thermal resistance (NDTR) [4,11], a phenomenon where the heat flux decreases as the applied temperature gradient increases. NDTR is used to design a thermal diode with a big rectification factor; it is also crucial for the functioning of some models of thermal transistors and logic gates [12]. There are attempts to explain the origin of NDTR (in systems given by the coupling of different lattices), see, e.g., the "phenomenological approach" in Ref. [13], but a general comprehensive understanding of the phenomenon is still lacking.

Hence, considering these central subjects for the heat mechanism study, we address here the following issues: (i) the development of new methods of modeling the heat conduction problem in anharmonic systems; (ii) the analytical investigation of the graded mass system as a reliable candidate for diode, different from that given by the coupling of different parts, whose rectification decays with the system size, and that is difficult to be constructed in practice; (iii) the understanding of NDTR onset and related properties, in particular, in a nonlinear system that is not the coupling of different lattices.

Here, we investigate graded anharmonic crystals with self-consistent reservoirs, details ahead, and show that graded materials are perfect candidates for diodes: their rectification does not decay with size (for certain mass distribution), they present NDTR, and may be constructed in practice [7]. We recall that rectification is absent in the classical harmonic version of this model [14]. Our analytical formalism makes transparent the mechanism behind these phenomena. Rectification occurs because the total heat flow involves a sum of "local conductivities," see Eqs. (4) and (5), each one depending on the local temperature (for the anharmonic system, not for the harmonic one) and also on the masses of neighbor particles. As we invert the system between two thermal baths, the distributions of masses and temperatures change in a different way, leading to a different heat flow—more comments ahead. For the NDTR onset, we have a competition between gradients of temperature and mass, see the denominator of the heat flow expression (4) and (5). For large gradients and anharmonicity, there is a change of the dominant term as we increase the temperature difference, and so, NDTR appears.

Let us introduce the model and our approach. We consider anharmonic crystals with stochastic reservoirs at each site. For simplicity, we take $d=1$. We will work with the "self-consistent condition," that means absence of heat flow between each inner reservoir and its site in the steady state, i.e., the inner reservoirs are not considered as "real" thermal baths as those given by the reservoirs at the boundaries: they describe only some residual mechanism of phonon scattering not present in the Hamiltonian. The use of these hybrid models is recurrent [15]. Precisely, we take N oscillators with Hamiltonian

$$H(q,p)=\sum_{j=1}^{N}\left[\frac{1}{2}\left(\frac{p_j^2}{m_j}+M_jq_j^2+\sum_{l\neq j}q_lJ_{lj}q_j\right)+\lambda\mathcal{P}(q_j)\right],$$

*emmanuel@fisica.ufmg.br

where $M_j>0$, $J_{jl}=J_{lj}$, $\mathcal{P}$ is the anharmonic on-site potential: $\mathcal{P}(q_j)=q_j^4/4$; with time evolution

$$dq_j=(p_j/m_j)dt, \quad dp_j=-(\partial H/\partial q_j)dt-\zeta_j p_j dt+\gamma_j^{1/2}dB_j, \tag{1}$$

where B_j are independent Wiener processes; ζ_j is the coupling between site j and its reservoir; and $\gamma_j=2\zeta_j m_j T_j$, where T_j is the temperature of the jth bath. Here, we will study only nearest-neighbor interactions.

The energy current inside the system is given by $\langle \mathcal{F}_{j\to}\rangle$, where $\langle\cdot\rangle$ means the expectation with respect to the noise distribution, and

$$\mathcal{F}_{j\to}=J_{j,j+1}(q_j-q_{j+1})\left(\frac{p_j}{2m_j}+\frac{p_{j+1}}{2m_{j+1}}\right), \tag{2}$$

precisely, $\mathcal{F}_{j\to}$ describes the heat flow from jth to $(j+1)$th site; details are found in previous works [16].

For ease of computation, we map our system on another with $m_j=1$, for all j. That is, we make the change of variables: $Q_j=\sqrt{m_j}q_j$, $P_j=p_j/\sqrt{m_j}$, and so, J, M and λ are replaced by $\tilde{J}_{jk}=(m_j)^{-1/2}J_{jk}(m_k)^{-1/2}$, $\tilde{\lambda}_j=\lambda_j/m_j^2$, $\tilde{M}_j=M_j/m_j$. We will drop out the tilde notation in the unit mass system below, but we make the rescale later to come back to the general system.

It is also useful to introduce the notation of the phase-space vector $\varphi=(Q,P)$, with $2N$ coordinates. Then, the dynamics [Eq. (1)] becomes $\dot{\varphi}=-A\varphi-\lambda\mathcal{P}'(\varphi)+\sigma\eta$, where $A=(A^0+\mathcal{J})$ and σ are $2N\times 2N$ matrices

$$A^0=\begin{pmatrix}0 & -I\\ \tilde{\mathcal{M}} & \Gamma\end{pmatrix},\quad \mathcal{J}=\begin{pmatrix}0 & 0\\ J & 0\end{pmatrix},\quad \sigma=\begin{pmatrix}0 & 0\\ 0 & \sqrt{2\Gamma\mathcal{T}}\end{pmatrix}.$$

I above is the unit $N\times N$ matrix; J is the $N\times N$ matrix for the interparticle interaction J_{lj}; $\tilde{\mathcal{M}},\Gamma,\mathcal{T}$ are diagonal $N\times N$ matrices: $\tilde{\mathcal{M}}_{jl}=M_j\delta_{jl}$, $\Gamma_{jl}=\zeta_j\delta_{jl}$, $\mathcal{T}_{jl}=T_j\delta_{jl}$. η are independent white noises; $\mathcal{P}'(\varphi)$ is a $2N\times 1$ matrix with $\mathcal{P}'(\varphi)_j=0$ for $j=1,\ldots,N$ and $\mathcal{P}'(\varphi)_i=d\mathcal{P}(\varphi_{i-N})/d\varphi_{i-N}$ for $i=N+1,\ldots,2N$. In what follows we use the index notation: i for index values in the set $[N+1,N+2,\ldots,2N]$, j for values in the set $[1,2,\ldots,N]$, and k for values in $[1,2,\ldots,2N]$.

In previous works [16] we establish an integral representation for the correlation functions, and so, for the heat current, of systems with the stochastic dynamics considered here. It starts with a Gaussian measure, related to the harmonic part of the interaction. Unfortunately, the analysis of the resulting formalism is still very intricate, in particular, for the case of hard anharmonic potentials. That is, it seems very difficult to reach the anharmonic behavior starting from perturbations of the harmonic part of the system. Then, in other previous work [17], we start an approximative scheme, that we conclude here, within this integral formalism in order to make it treatable.

Let us describe our approach. Now, we first consider the equations of dynamics without the interparticle interaction J, but with the anharmonic on-site potential. We do not know a strong solution for the decoupled anharmonic problem, but we know the steady distribution: we follow Boltzmann, i.e., our system with $J=0$ involves only noninteracting particles, each one connected to a thermal bath, and so we have, in the notation Q,P,

$$d\mu_*(Q,P)=\exp\left(-\sum_{j=1}^{N}H_j^{(J=0)}/T_j\right)\prod_j dQ_j dP_j/\text{norm.},$$

$$H_j^{(J=0)}=\left(\frac{1}{2}M_jQ_j^2+\lambda_j\mathcal{P}(Q_j)+\frac{1}{2}P_j^2\right).$$

To turn on J, we use the Girsanov theorem, which relates the solution of the complete process φ (with J, the interparticle interaction) with the previous one ϕ (with $J=0$). Precisely, it states that, for $t_1,\ldots,t_k\le t$, $\langle\varphi_{r_1}(t_1)\cdots\varphi_{r_k}(t_k)\rangle=\int\phi_{r_1}(t_1)\cdots\phi_{r_k}(t_k)Z(t)d\mu$, where $\langle\cdot\rangle$ is the expectation for the complete process φ, $d\mu$ is the distribution associated to the expectations of ϕ (the decoupled process), and the "corrective" factor $Z(t)$ is given by, after manipulations involving Itô calculus [16,17],

$$\begin{aligned}Z(t)=\exp[&-\gamma_i^{-1}\phi_i(t)\mathcal{J}_{ij}\phi_j(t)\\&+\gamma_i^{-1}\phi_i(0)\mathcal{J}_{ij}\phi_j(0)]\exp\left(\int_0^t ds\,\gamma_i^{-1}\phi_i(s)\mathcal{J}_{ij}\phi_{j+N}(s)\right.\\&-\int_0^t ds\,\phi_j(s)\mathcal{J}_{ji}^{\dagger}\gamma_i^{-1}A_{ik}^0\phi_k(s)\\&-\int_0^t ds\,\phi_j(s)\mathcal{J}_{ji}^{\dagger}\gamma_i^{-1}\lambda\mathcal{P}'(\phi)_i(s)\\&\left.-\frac{1}{2}\int_0^t ds\,\phi_j(s)\mathcal{J}_{ji}^{\dagger}\gamma_i^{-1}\mathcal{J}_{ij}\phi_j(s)\right).\end{aligned} \tag{3}$$

We assume the boundary condition $\phi(0)=0$, for simplicity. In the steady state, the heat flow [Eq. (2)] is related to the expression $\lim_{t\to\infty}\langle\varphi_u(t)\varphi_v(t)-\varphi_{u-N}(t)\varphi_{v+N}(t)\rangle$, $u>N, v\le N$, i.e., $\int\phi_u(t)\phi_v(t)Z(t)d\mu$, etc. Writing $Z(t)=\exp[-\int W(\phi(s)]ds$, in a perturbative analysis, we stay with terms such as $\int\{\phi_u(t)\phi_v(t)W[\phi(s)]\}ds\,d\mu$. But we do not know the distribution $d\mu$, that is very hard to calculate: for the nonlinear process we know only the steady distribution $d\mu_*$. Then, we introduce an approximative scheme.

First, to relate the fields $\phi(t)$ and $\phi(s)$, we use the Itô calculus which establishes that, for functions of ϕ: $\langle f[\phi(t)]\rangle=e^{-t\mathcal{H}}f[\phi(0)]$, $\mathcal{H}=-\frac{1}{2}\gamma_i\nabla_i^2+[A^0\phi+\lambda\mathcal{P}'(\phi)]\cdot\nabla$, where ∇ means the derivation in relation to ϕ (the index i, as well known, takes values in $[N+1,\ldots,2N]$). The difference between the linear and nonlinear dynamics in the generator of the time evolution $\mathcal{H}$ above is in the term multiplying the gradient operator: precisely, instead of $A^0\phi$ we have $[A^0+\lambda\mathcal{P}'(\phi)/\phi]\phi$. Thus, to make easier the calculations, we replace $\phi(t)$ by its average value. Moreover, in the exponential relaxation of ϕ, we still replace $\mathcal{P}'(\phi)/\phi$ by its average value, more details ahead. All together means: $\phi(t)\to e^{-(t-s)\mathcal{H}}\phi(s)=e^{-(t-s)\mathcal{A}}\phi(s)$, where $\mathcal{A}$ is given by A^0 with M

replaced by $\mathcal{M} \equiv M + \langle \lambda \mathcal{P}'(\phi)/\phi \rangle$. We still have a problem: the computation of $\int \phi(s)\phi(s) d\mu$ is not possible, since we do not know the distribution $d\mu$, as said before. Considering that we have an exponential convergence to the steady state, and so, the main terms involve s close to t, we propose to replace $d\mu$ by $d\mu_*$, the well known steady distribution.

To summarize, our main approximations mean the replacement of $\phi(t)$ by $\langle \phi(t) \rangle$ and $d\mu$ by $d\mu_*$; after it, the expression for the heat flow will involve terms such as

$$\int d\tau \int d\mu_* (e^{-\tau \mathcal{A}}\phi)(e^{-\tau \mathcal{A}}\phi) W(\phi),$$

where the time dependence is carried only by $\exp(-\tau \mathcal{A})$, where τ comes from $t-s$, and, as $t \to \infty$, $\tau \in [0,\infty]$.

In order to test our approximative scheme, we first turn to the harmonic self-consistent chains, where rigorous results are known. For a system with particles with the same mass, and for the case of weak interparticle interactions, up to first order in $\mathcal{J}$, we have

$$\lim_{t\to\infty} \langle \varphi_u(t)\varphi_v(t) \rangle = \lim_{t\to\infty} \int \phi_u(t)\phi_v(t) Z(t) d\mu$$
$$\simeq \int \phi_u \phi_v [-\gamma_i^{-1} \phi_i \mathcal{J}_{ij} \phi_j] d\mu_*$$
$$+ \int (e^{-\tau A^0}\phi)_u (e^{-\tau A^0}\phi)_v \times \{\gamma_i^{-1}\phi_i \mathcal{J}_{ij}\phi_{j+N}$$
$$- \phi_j \mathcal{J}_{ji}^\dagger \gamma_i^{-1} A_{ik}^0 \phi_k\} d\tau d\mu_*,$$

where $\tau \in [0,\infty]$. After the τ and ϕ integrations, we get $\lim_{t\to\infty} \mathcal{J}_{uv} \langle \varphi_u(t)\varphi_v(t) \rangle = (\mathcal{J}_{uv})^2 (2\zeta M)^{-1}(T_u - T_v)$. That is exactly the same value, considering the lower order in the interparticle interaction, of the rigorous computation [16]. This expression leads us to the correct thermal conductivity. Moreover, for the case of a chain with particles with alternate masses (two different values), our scheme also works perfectly well: it gives, again, the same value of the rigorous computation.

Let us, now, analyze our anharmonic crystal. Considering first order in J, with the integration in τ carried out after using a representation for $e^{-\tau \mathcal{A}}$ [16], we get, for $u > N, v \leq N$,

$$\langle \varphi_u \varphi_v \rangle = -(2\zeta_u T_u)^{-1} \mathcal{J}_{uv} \langle \phi_u^2 \phi_v^2 \rangle + (\mathcal{M}_v - \mathcal{M}_u)(D_{uv})^{-1}(\gamma_u^{-1} + \gamma_v^{-1}) \mathcal{J}_{uv} \langle \phi_u^2 \phi_{v+N}^2 \rangle + \frac{\zeta_u + \zeta_v}{D_{uv}} [\mathcal{M}_u \zeta_v \gamma_v^{-1} \langle \phi_{u-N}^2 \phi_{v+N}^2 \rangle$$
$$- \mathcal{M}_v \zeta_u \gamma_u^{-1} \langle \phi_u^2 \phi_v^2 \rangle] \mathcal{J}_{vu}^\dagger + \frac{\mathcal{M}_u}{D_{uv}} [(\mathcal{M}_u - \mathcal{M}_v) + \zeta_v(\zeta_u + \zeta_v)] \{(M_u \gamma_u^{-1} + M_v \gamma_v^{-1}) \langle \phi_{u-N}^2 \phi_v^2 \rangle \mathcal{J}_{uv}^\dagger + [\lambda_{u-N} \langle \phi_{u-N} \mathcal{P}'(\phi_{u-N}) \phi_v^2 \rangle \gamma_u^{-1}$$
$$+ \lambda_v \langle \phi_{u-N}^2 \mathcal{P}'(\phi_v) \phi_v^2 \rangle \gamma_v^{-1}] \mathcal{J}_{vu}^\dagger \}, \quad (4)$$

where $\mathcal{M}_u \equiv \mathcal{M}_{u-N}$, $D_{uv} = (\mathcal{M}_u - \mathcal{M}_v)^2 + (\mathcal{M}_u \zeta_v + \mathcal{M}_v \zeta_u)(\zeta_u + \zeta_v)$. For $u > N$, $\langle \phi_u^2 \rangle = T_u$; but the computation of $\langle \phi_v^2 \rangle$, $v \leq N$, is not easy (note that $d\mu_*$ is a single variable distribution, and so, $\langle \phi_u^k \phi_v^m \rangle = \langle \phi_u^k \rangle \langle \phi_v^m \rangle$). Let us assume some regime before any approximation: we consider a high anharmonic system, i.e., λ large and M small. Thus, we take $\langle \phi_v^2 \rangle = 2c_1 T_v^{1/2}/\lambda_v^{1/2}$, $\langle \phi_v^4 \rangle = 4c_2 T_v/\lambda_v$. If $M=0$, we would have $c_1 \simeq \Gamma(3/4)/\Gamma(1/4) \simeq 1/3$, $c_2 \simeq \Gamma(5/4)/\Gamma(1/4) = 1/4$. To determine the values of c_1 and c_2, we turn to the expression of the heat current $\mathcal{F}_{j\to} = \mathcal{J}_{uv}(\langle \phi_u \phi_v \rangle - \langle \phi_{u-N} \phi_{v+N} \rangle)/2$, with $u-N = j$, $v = j+1$, take all sites at the same temperature T and find the values such that $\mathcal{F}_{j\to} = 0$. We obtain $c_2 = 1/4$ and $c_1 = 1/2$. Then, we perform the further computations. For high anharmonicity and very small temperatures, for the dominant term in $\mathcal{F}_{j\to} \equiv \mathcal{F}_{j,j+1}$, we obtain, after the rescaling back to the system with general mass values, i.e., $\lambda_j \to \lambda_j/m_j^2$, etc.,

$$\mathcal{F}_{j,j+1} = J^2 \zeta [m_j m_{j+1} D_{j,j+1}]^{-1} (T_j - T_{j+1})$$
$$\simeq J^2 [\lambda^{1/2} \zeta (m_{j+1} T_j^{1/2} + m_j T_{j+1}^{1/2})]^{-1} (T_j - T_{j+1}), \quad (5)$$

where we take, after the rescale, uniform potentials and couplings: $\lambda_j = \lambda$, etc. From $\mathcal{F}_{j,j+1}$ above and the self-consistent condition $\mathcal{F} = \mathcal{F}_{1,2} = \mathcal{F}_{3,4} = \cdots = \mathcal{F}_{N-1,N}$, which establishes that the heat current comes from the first reservoir, passes through the chain and goes out by the last reservoir, we determine the temperature profile. We have

$$\mathcal{F}(m_2 T_1^{1/2} + m_1 T_2^{1/2})/\mathcal{C} = T_1 - T_2 = \cdots,$$

$$\mathcal{F}(m_N T_{N-1}^{1/2} + m_{N-1} T_N^{1/2})/\mathcal{C} = T_{N-1} - T_N,$$

where $\mathcal{C} = J^2/\lambda^{1/2}\zeta$. We sum all the equations to obtain

$$\mathcal{F}\{(m_2 T_1^{1/2} + (m_1 + m_3) T_2^{1/2} + \cdots + (m_{N-2} + m_N) T_{N-1}^{1/2}$$
$$+ m_{N-1} T_N^{1/2}\}/\mathcal{C} = T_1 - T_N,$$

that gives us, from $\mathcal{F} = \mathcal{K}(T_1 - T_N)/(N-1)$, an expression for the thermal conductivity $\mathcal{K}$. The system of equations above may be rewritten as

$$\frac{T_1 - T_2}{m_2 T_1^{1/2} + m_1 T_2^{1/2}} = \cdots = \frac{T_{N-1} - T_N}{m_N T_{N-1}^{1/2} + m_{N-1} T_N^{1/2}}.$$

For the case of particles with the same mass, the equations become $T_1^{1/2} - T_2^{1/2} = \cdots = T_{N-1}^{1/2} - T_N^{1/2}$, that leads to a linear profile for $T^{1/2}$, i.e., $T_k^{1/2}=T_1^{1/2}+[(k-1)/(N-1)](T_N^{1/2}-T_1^{1/2})$. For a general mass distribution, the problem is more complicated: let us examine it in the case of a small temperature gradient. We write $T_1=T+a_1\epsilon$ and $T_N=T+a_N\epsilon$; T,a_1,a_N and ϵ given (ϵ small). Then, T_j is a function of ϵ, with values between T_1 and T_N: $T_j=T+a_j\epsilon+\mathcal{O}(\epsilon^2)$. Let us analyze only the first order in ϵ. From the equations for the self-consistent condition, we get the solution $a_j=a_1+(a_1-a_N)\mathcal{S}_j/\mathcal{S}_N$, $\mathcal{S}_j=m_1+2m_2+\cdots+2m_{j-1}+m_j$. Hence, turning to the thermal conductivity formula, after algebraic manipulations, we obtain

$$\frac{1}{\mathcal{K}}-\frac{1}{\mathcal{K}'}=\frac{\epsilon(a_1-a_N)}{\mathcal{C}(N-1)2T^{1/2}\mathcal{S}_N}[m_N^2-m_1^2],$$

where $\mathcal{K}'$ is the conductivity for the system with inverted boundary baths. And so, there is rectification even for a small gradient of temperature. And more, if the graded mass grows with N^2, i.e., $m_j=j^2\cdot m_1$, then rectification does not decay with N. By taking $T_N>T_1$ (i.e., $a_N>a_1$) and $m_N>m_1$, we see that the thermal conductivity is bigger when heat flows from the large to the small mass, as experimentally observed in a graded system [7].

We stress here that the dependence on temperature for the local anharmonic conductivity comes from the dynamics: $\langle\phi(t)\rangle\sim e^{(-t\mathcal{A})}\phi(0)$, where $\mathcal{A}$ depends on T for the anharmonic (not for the harmonic) case. The combination of particle masses and temperatures, and the difference as we invert the chain, lead to rectification.

Now, we consider the investigation of NDTR. We turn to Eq. (4), that is directly related to the heat flow, and is valid for weak interparticle interaction J in any regime: low and high anharmonicity, temperature, etc. All the terms include D in the denominator, except the first one that, however, may be manipulated and absorbed by the other terms. Hence, $\mathcal{F}_{j\rightarrow}$ will have $D_{j,j+1}$ in the denominator (see, e.g., the first equality in Eq. (5), the expression for high anharmonic regime), where, we recall, $D_{j,j+1}=(\mathcal{M}_j-\mathcal{M}_{j+1})^2+2\zeta^2(\mathcal{M}_j+\mathcal{M}_{j+1})$, $\mathcal{M}_j=M_j+\langle\lambda_j\phi_j^2\rangle$, expression determined for a system with unit masses. For high anharmonicity we have $\langle\lambda_j\phi_j^2\rangle\sim T_j^{1/2}/\lambda_j^{1/2}$; and for very low anharmonicity, $\langle\lambda_j\phi_j^2\rangle\sim\lambda_jT_j/M_j$. Rescaling to get the expression for a system with different values for the particle masses, and considering high anharmonicity, just to fix the expression for the temperature behavior (but the analysis below, adjusting the power of T, follows anywhere), we have, for the first term in $D_{j,j+1}$

$$(\mathcal{M}_j-\mathcal{M}_{j+1})^2=(c_jm_{j+1}-c_{j+1}m_j)^2/(m_jm_{j+1})^2,$$

$c_j=[M+\lambda^{1/2}T_j^{1/2}]$. The second term in D always increases with T, and is subdominant for ζ small; note however that it shall dominate for very small T, as assumed in the second part of Eq. (5). Let analyze the first term, considering a graded mass chain. For $m_{j+1}>m_j$ and $T_{j+1}>T_j$, i.e., gradient of mass and temperature at the same direction, if $\Delta T_j=T_{j+1}-T_j\ll\Delta m_j=m_{j+1}-m_j$, then $c_jm_{j+1}>c_{j+1}m_j$; and if $\Delta T_j\gg\Delta m_j$, then $c_jm_{j+1}<c_{j+1}m_j$. Recall that ΔT_j increases as we increase T_j, and, of course, ΔT_j depends also on T_1-T_N, the "total gradient": ΔT_j will be very small if $|T_1-T_N|$ is very small. Hence, starting from a very low total temperature gradient ΔT, as we increase ΔT, then $(\mathcal{M}_j-\mathcal{M}_{j+1})^2$ first decreases, but after same point it becomes an increasing function. That is, $1/D$ first increases and, in sequel, decreases with ΔT. As we have $\mathcal{F}=\mathcal{F}_j\sim D^{-1}\Delta T_j$, and D changes as $\tilde{c}\Delta T_j^{1/2}$, with $\tilde{c}$ depending on $\lambda,\Delta m_j$, if λ and Δm_j are not very small, then $\tilde{c}\Delta T_j^{1/2}$ dominates ΔT_j ($T_j<1$), and the heat current first increases and then decreases with ΔT. In other words, we have NDTR.

To conclude, we stress that diodes of graded materials sound to be experimentally reliable [7], and ubiquitous structures: our results follow for many other anharmonic potentials as indicated by the formalism derivation.

This work was supported by CNPq and Fapemig (Brazil).

[1] S. Lepri, R. Livi, and A. Politi, Phys. Rep. **377**, 1 (2003); A. Dhar, Adv. Phys. **57**, 457 (2008).
[2] M. Terraneo, M. Peyrard, and G. Casati, Phys. Rev. Lett. **88**, 094302 (2002).
[3] B. Hu, L. Yang, and Y. Zhang, Phys. Rev. Lett. **97**, 124302 (2006).
[4] B. Li, L. Wang, and G. Casati, Phys. Rev. Lett. **93**, 184301 (2004).
[5] N. Yang *et al.*, Appl. Phys. Lett. **95**, 033107 (2009); **93**, 243111 (2008).
[6] D. Segal and A. Nitzan, Phys. Rev. Lett. **94**, 034301 (2005); L.-A. Wu and D. Segal, *ibid.* **102**, 095503 (2009).
[7] C. W. Chang *et al.*, Science **314**, 1121 (2006).
[8] J. P. Eckmann C. Mejia-Monasterio, Phys. Rev. Lett. **97**, 094301 (2006).
[9] G. Casati, C. Mejia-Monasterio, and T. Prosen, Phys. Rev. Lett. **98**, 104302 (2007).
[10] N. Yang, N. Li, L. Wang, and B. Li, Phys. Rev. B **76**, 020301(R) (2007).
[11] B. Hu, D. He, L. Yang, and Y. Zhang, Phys. Rev. E **74**, 060101(R) (2006).
[12] B. Li *et al.*, Appl. Phys. Lett. **88**, 143501 (2006); L. Wang and B. Li, Phys. Rev. Lett. **99**, 177208 (2007).
[13] D. He, S. Buyukdagli, and B. Hu, Phys. Rev. B **80**, 104302 (2009).
[14] E. Pereira and H. C. F. Lemos, Phys. Rev. E **78**, 031108 (2008); D. Segal, *ibid.* **79**, 012103 (2009).
[15] F. Bonetto, J. L. Lebowitz, J. Lukkarinen, and S. Olla, J. Stat. Phys. **134**, 1097 (2009).
[16] E. Pereira and R. Falcao, Phys. Rev. E **70**, 046105 (2004); Phys. Rev. Lett. **96**, 100601 (2006).
[17] E. Pereira, Physica A **388**, 4695 (2009).