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Heat conductivity of a perturbed monatomic Toda lattice without impurities

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Abstract. The problem of thermal conduction in a perturbed one-dimensional Toda lattice is investigated within the framework of non-equilibrium thermodynamics. The intrinsic thermal resistance of the lattice is due to its anharmonicity with the dominant contributing mechanism involving soliton–phonon interactions. Our calculations indicate that the coefficient of heat conduction is exceedingly small at both very low and very high temperatures and exhibits an expected maximum in the intermediate temperature range.

1. Introduction

The on-going search for physical (especially lattice dynamics) models that would exhibit the Fourier heat law (FHL) is, as stated by Peierls [1], one of the outstanding unsolved problems of modern physics. This gives a strong motivation to undertake the present study. Let us recall here that even systems obeying the FHL can transport energy in the form of slowly decaying coherent excitations such as sound-like pulses and solitary waves. For an up-to-date review of the literature on the topic of heat waves as thermal energy carriers, the reader is referred to the excellent survey by Joseph and Preziosi [2].

Toda [3] has emphasized the importance of lattice anharmonicity and solitons for mechanisms of heat energy flow in electrically non-conducting crystals. Thermal resistance of such materials arises as a result of a number of contributions, for example due to dislocations, point defects, external boundaries with heat reservoirs and a host of other imperfections. On the other hand, in perfect crystals, two types of processes can be distinguished. First, so-called normal processes are defined as such where the total momentum of lattice phonons is conserved. For this reason they cannot contribute to thermal resistance since this implies a continued energy flow. Then, there are the so-called Umklapp processes, for which the total momentum is not conserved since a portion of the phonon momentum is transferred to the lattice. These types of processes contribute significantly to the overall thermal resistance of the lattice.

It has been demonstrated [4] that the thermal conductivity of a monatomic harmonic lattice is infinite (zero resistance) since the temperature gradient across the lattice vanishes. This is in contrast to a perfect anharmonic lattice (for example, with a Lennard-Jones intersite potential), whose conductivity stays finite. Keeping the concentration of isotopic

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impurities in the anharmonic lattice constant, it can be seen that anharmonicity always increases the resultant thermal conductivity. It should be emphasized that, even in the idealized situation of a perfect crystal free from any defects and impurities, anharmonicity of the restoring lattice forces would produce intrinsic thermal resistance through Umklapp and other contributing mechanisms.

However, difficulties exist in the experimental determination of the relative contributions from the non-linear mechanisms discussed above. This is due to the fact that only very few crystals can be considered perfect enough that their intrinsic thermal resistance is not overshadowed by effects due to imperfections [5].

The main objective of the present paper is to investigate a perturbed Toda lattice as a tractable example of a non-linear lattice and to examine the role of solitons and phonons in thermal resistance processes. The reader is referred to an important review paper by Mertens and Büttner [6] for information regarding Toda lattices, their classical and quantum properties including statistics, and thermal conductivity. In this context, it should be emphasized that both the classical [7] and the quantum [8] Toda lattices have been shown to be completely integrable. This means that all its modes of behaviour are autonomous and no thermalization is possible through their collisions leading to zero thermal resistance. A diatomic Toda lattice, however, is not integrable and, as a consequence, thermal resistance has been seen in numerical simulations [9]. There is still a need to investigate the origin of thermal resistance in monatomic lattices. Our approach to this problem will be to treat the lattice as a nearly perfect monatomic Toda lattice and focus on the relaxation processes of Toda solitons (TS) off the 'clouds' of phonons. The working assumption will be that deviations from complete integrability, in the form of quantum excitations and their interactions with Toda solitons, give rise to finite lifetimes, and hence thermal resistance. The Hamiltonian will be constructed as having classical Toda contributions as well as quantum corrections that are relatively small but nevertheless lead to an eventual decay of solitons. Our calculations will be carried out in the framework of the non-equilibrium statistical operator technique (NSOT) [10, 11]. Although, Kubo's linear response method was also successfully used for the same purpose [12], Zubarev's NSOT technique appears to be more convenient in the present context.

In contrast to a majority of papers dealing with this type of problem, we decided not to regard the chain as having a finite length. This approach helped us to avoid the problem of boundary conditions and the associated temperature discontinuity at both ends [12]. Also, this is more amenable to analytical calculations.

This paper is organized as follows. In section 2 we outline the most fundamental properties of the classical Toda model. This is followed in section 3 by the preparation of the Toda Hamiltonian to a form amenable to subsequent perturbation calculations involving quantum effects. We decompose the Hamiltonian into distinct parts in terms of classical and quantum degrees of freedom as well as their interactions. In section 4 the density matrix of NSOT is formulated and then the average energy flux is calculated. Consequently, we extract the heat conduction coefficient in functional form. Finally, in section 5 we provide a discussion of the obtained results.

2. The classical Toda lattice

Consider a classical Toda lattice of identical molecules located periodically along the x axis with equilibrium distance R_0 between neighbouring sites. The nearest-neighbour interaction potential U (the Toda potential) is expressed by

$$U = (\chi/b)[\![u_n - u_{n-1} + (1/b)\{\exp[b(u_{n-1} - u_n)] - 1\}]\!]. \tag{2.1}$$

The equation of motion for lattice masses is given by Newton's second law with the associated force given by

$$f_n = -\partial U/\partial u_n \tag{2.2}$$

or, explicitly,

$$M\,\mathrm{d}^2u_n/\mathrm{d}t^2 = (\chi/b)[\exp(bu_n) - \exp(bu_{n+1})] \tag{2.3}$$

where M denotes the molecular mass and u_n the displacement of the nth molecule. Here, the parameter χ represents the longitudinal elasticity coefficient of the corresponding harmonic chain while b denotes the magnitude of anharmonicity.

Introducing the relative displacement as

$$\rho_n \equiv u_{n-1} - u_n$$

the equation of motion becomes

$$M\,\mathrm{d}^2\rho_n/\mathrm{d}t^2 = (\chi/b)[\exp(b\rho_{n+1}) + \exp(b\rho_{n-1}) - 2\exp(b\rho_n)]. \tag{2.4}$$

A one-soliton solution (TS) of the Toda lattice problem is then found as

$$\exp(b\rho_n) - 1 = \sinh^2(\mu)/\cosh^2[(\mu/R_0)(nR_0 - vt)] \tag{2.5}$$

which describes a compressional pulse [10] propagating along the chain with velocity v that determines the parameter μ through the relationship

$$v/c = \sinh(\mu)/\mu \tag{2.6}$$

and $c \equiv R_0(\chi/M)^{1/2}$ is the longitudinal sound velocity of the corresponding harmonic chain (i.e. for $b = 0$). The coefficient μ is called the solitonic parameter and it defines the solitonic domain of localization (width) through: $\Delta n = 2\pi/\mu$. It is evident from equation (2.6) that the TS propagation velocity v always exceeds the sound velocity ($v > c$). Moreover, TS with larger amplitudes (and hence with larger parameters μ) propagate faster.

The lattice contraction between adjacent molecules, which is associated with the formation of a simple TS, can be calculated directly from equation (2.5) as

$$\rho_n(t) = (1/b)\ln\{1 + \sinh^2(\mu)/\cosh^2[(\mu/R_0)(nR_0 - vt)]\}. \tag{2.7}$$

Provided the continuum approximation is applicable (i.e. that $\Delta n \gg 1$ or equivalently that $\mu \ll 2\pi$), equation (2.7) may be simplified as

$$\rho(x,t) = (1/b)\sinh^2(\mu)/\cosh^2(\mu\xi/R_0) \tag{2.8}$$

where we have introduced a moving coordinate $\xi \equiv x - x_0 - vt$ with x_0 representing the position of the TS centre. In equation (2.8), $\rho(x,t)$ replaced the discrete variable ρ_n and, in the continuum limit, is given by

$$\rho(x,t) = -R_0\partial u(x,t)/\partial x. \tag{2.9}$$

This enables us to integrate equation (2.8) for $u(x, t)$ using the asymptotic boundary condition $u(\infty) = 0$, which yields [13]

$$u(\xi) = \frac{2[1 - \tanh(\mu\xi/R_0)]\sinh^2(\mu)}{3b\mu^2[1 + 2\cos^2(\mu\xi/R_0)]}. \tag{2.10}$$

The effective mass of a Toda soliton M^* is defined through the change of the lattice mass density due to lattice site displacements. For the solution of equation (2.7), M^* has the simple form [14]

$$M^* = 2\mu M. \tag{2.11}$$

The energy of a single TS is given by

$$E_s = (2\chi/b^2)[\sinh(\mu) - \mu] \tag{2.12}$$

which, in the long-wavelength approximation, can be represented as the sum of the potential (E_0) and the kinetic energies:

$$E_s \simeq E_0 + \tfrac{1}{2}M^* v^2. \tag{2.13}$$

3. Perturbation of the Hamiltonian

The one-dimensional Toda lattice Hamiltonian can be written as

$$H = \sum_n \left[\frac{p_n^2}{2M} + \frac{\chi}{b}\left(-\rho_n + \frac{1}{b}[\exp(b\rho_n) - 1]\right)\right] \tag{3.1}$$

where $p_n \equiv M\partial u_n/\partial t$ represents the momentum variable conjugate to the displacement u_n. As we have already mentioned, a perfect Toda lattice is completely integrable and hence no thermal resistance is present. However, we can use the Toda Hamiltonian as a starting point for the modelling of a more realistic behaviour of monatomic lattices. To this end, we perturb this classical Hamiltonian by introducing quantum oscillations superimposed on the (integrable) classical motion of the chain's masses. This procedure will make the Hamiltonian nearly integrable and the resultant interactions between classical modes (solitons) and quantum modes (phonons) will lead to scattering giving finite lifetimes to solitons and resulting in a finite thermal resistance of the lattice. Thus, we represent the position and momentum variables as composed of classical and quantum contributions as follows:

$$u_n = u_n^{\mathrm{cl}} + \mu_n^{\mathrm{qu}} \equiv \beta_n + U_n \qquad \text{or} \qquad \rho_n = \rho_n^{\mathrm{cl}} + \rho_n^{\mathrm{qu}} \tag{3.2}$$

and

$$p_n^{\mathrm{cl}} = \pi_n \qquad p_n^{\mathrm{qu}} = P_n \tag{3.3}$$

where we have introduced the second set of symbols for greater clarity. This type of representation has already proven useful when discussing the Mössbauer effect in a Toda lattice [14]. With equations (3.2) and (3.3), the Hamiltonian of equation (3.1) takes the form

$$H = \sum_n \left(\frac{P_n^2}{2M} + \frac{\chi}{2}(U_{n-1} - U_n)^2 \right) + \sum_n \left[\frac{\pi_n^2}{2M} + \frac{\chi}{b}\left(-(\beta_{n-1} - \beta_n) + \frac{1}{b}\{\exp[b(\beta_{n-1} - \beta_n)] - 1\} \right) \right] + \sum_n \{\exp[b(\beta_{n-1} - \beta_n)] - 1\} \left(\frac{\chi}{b}\rho_n + \frac{\chi}{2}\rho_n^2 \right) + \sum_n \frac{\pi_n P_n}{M}. \tag{3.4}$$

The first of the summations above represents the energy of the phonon degrees of freedom and can be readily second quantized using the standard transformations below:

$$U_n = \frac{1}{\sqrt{N}} \sum_q \left(\frac{\hbar}{2M\Omega_q} \right)^{1/2} \exp(\mathrm{i}nR_0 q)(a_q + a_{-q}^+) \tag{3.5}$$

and

$$P_n = -\mathrm{i}\frac{1}{\sqrt{N}} \sum_q \left(\frac{\hbar M \Omega_q}{2} \right)^{1/2} \exp(-\mathrm{i}nR_0 q)(a_q^+ - a_{-q}). \tag{3.6}$$

As a result, we obtain the diagonalized form

$$H_{\mathrm{ph}} = \sum_k \hbar\Omega_k (a_k^+ a_k + \tfrac{1}{2}) \tag{3.7}$$

where a_k^+ and a_k denote the creation and annihilation operators, respectively, for phonons with the wavenumber k which satisfy the dispersion relation $\Omega_k = (\chi/M)^{1/2}k$.

The second sum in equation (3.4) describes the classical part of lattice vibrations, which are required for TS formation, i.e.

$$H_{\mathrm{sol}} = \sum_n \left[\frac{\pi_n^2}{2M} + \frac{\chi}{b}\left(-(\beta_{n-1} - \beta_n) + \frac{1}{b}\{\exp[b(\beta_{n-1} - \beta_n)] - 1\} \right) \right]. \tag{3.8}$$

The remaining part of the Hamiltonian in equation (3.4) represents interactions between TS and quantized phonons, i.e.

$$H_{\mathrm{int}} = \frac{\chi}{b^2} \sum_n \{\exp[b(\beta_{n-1} - \beta_n)] - 1\} \Bigg(\frac{1}{2}\sum_q |\alpha_q^n|^2 + \sum_n (\alpha_q^n a_q + \alpha_q^{n*} a_q^+) + \frac{1}{2}\sum_q \sum_{q'} (2\alpha_q^{n*}\alpha_{q'}^n a_q^+ a_{q'} + \alpha_q^n \alpha_{q'}^n a_q a_{q'} + \alpha_q^{n*}\alpha_{q'}^n a_q^+ a_{q'}^+) \Bigg) + \sum_n \sum_q \frac{1}{M}\pi_n (\gamma_q^{n*} a_q^+ + \gamma_q^n a_q) \tag{3.9}$$

where the following coefficients have been used

$$\alpha_q^n = b\left(\frac{\hbar}{2MN\Omega_q} \right)^{1/2} [\exp(-\mathrm{i}qR_0) - 1] \exp(+\mathrm{i}qnR_0) = \alpha_q \exp(+\mathrm{i}qnR_0) \tag{3.10}$$

and

$$\gamma_q^n = -\mathrm{i}N^{-1/2}(\hbar M\Omega_q/2)^{1/2}\exp(+\mathrm{i}nR_0q). \tag{3.11}$$

The last term in the interaction Hamiltonian of equation (3.9) is inconvenient as it stands. However, denoting it as

$$H_{\mathrm{int}}^{(2)} = \sum_n\sum_q \frac{1}{M}\pi_n(\gamma_q^{n^*}a_q^+ + \gamma_q^n a_q) \tag{3.12}$$

we can effectively remove it from the Hamiltonian by performing a unitary transformation of the form

$$H_{\mathrm{eff}} = \mathrm{e}^{-S}(H_{\mathrm{ph}} + H_{\mathrm{sol}} + H_{\mathrm{int}}^{(2)})\mathrm{e}^{+S} \tag{3.13}$$

where the operator S is chosen as

$$S = \sum_q(X_qa_q - X_q^*a_q^+). \tag{3.14}$$

The *a priori* unknown amplitudes X_q can be determined from the condition

$$H_{\mathrm{int}}^{(2)} - [S, H_{\mathrm{ph}} + H_{\mathrm{sol}} + H_{\mathrm{int}}^{(2)}] = 0 \tag{3.15}$$

and they are, indeed, found to be

$$X_q = (\hbar\Omega_qM)^{-1}\sum_n\pi_n\gamma_q^n. \tag{3.16}$$

From the definitions used we obtain the conjugate momentum as

$$\pi_n = M\partial\beta_n/\partial t = -Mv\partial\beta/\partial x \tag{3.17}$$

but we also know that

$$\beta_{n-1} - \beta_n \simeq -R_0\partial\beta/\partial x = \rho(x,t) \tag{3.18}$$

provided the continuum approximation is valid. Therefore, in view of equation (2.8) we obtain

$$\pi_n = \left(\frac{Mv}{R_0b}\right)\frac{\sinh^2(\mu)}{\sinh^2[(\mu/R_0)(nR_0 - x_0 - vt)]} \tag{3.19}$$

which can be inserted into equation (3.16). Then, replacing the summation $\sum_n$ by the integration $(1/R_0)\int_{-\infty}^{\infty}\mathrm{d}x$, we obtain explicitly the form of the required coefficient X_q as

$$X_q = \frac{\pi v}{\hbar b}\left(\frac{\gamma_q}{\Omega_q}\right)\left(\frac{\sinh(\mu)}{\mu}\right)^2 q\frac{\exp[\mathrm{i}(x_0+vt)q]}{\sinh(\pi R_0q/2\mu)}. \tag{3.20}$$

Next, we determine the form of the remainder of the interaction Hamiltonian following the unitary transformation discussed above:

$$H_{\rm int}^{\rm eff} = {\rm e}^{-S} H_{\rm int}^{(1)} {\rm e}^{+S} = \frac{\chi}{b^2} \sum_n \{\exp[b(\beta_{n-1} - \beta_n)] - 1\}$$
$$\times \left(E_0 + \sum_q \alpha_q^n a_q + \sum_q \alpha_q^{n^*} a_q^+ + \sum_{q,q'} \alpha_q^{n^*} \alpha_{q'}^n a_q^+ a_{q'} + \frac{1}{2} \sum_{q,q'} \alpha_q^n \alpha_{q'}^n a_q a_{q'} + \frac{1}{2} \sum_{q,q'} \alpha_q^{n^*} \alpha_{q'}^{n^*} a_q^+ a_{q'}^+ \right) \tag{3.21}$$

where E_0 is an insignificant constant energy shift given below as

$$E_0 = \frac{1}{2} \sum_{q,q'} (2\alpha_q^{n^*} \alpha_{q'}^n X_q X_{q'}^* + \alpha_q^n \alpha_{q'}^n X_q^* X_{q'}^* + \alpha_q^{n^*} \alpha_{q'}^{n^*} X_q X_{q'}). \tag{3.22}$$

Thus, the transformations used in this section have led us to a more convenient form of the Hamiltonian, which includes a classical (soliton) part, a quantum (phonon) part and their mutual interactions. The latter part has been represented effectively by equation (3.21) where coupling to soliton momenta has been explicitly removed.

4. Calculations of the energy flux

Our starting point is the effective Hamiltonian obtained in section 3, i.e.

$$H_{\rm tot} = H_{\rm sol} + H_{\rm ph} + H_{\rm int}^{\rm eff} \tag{4.1}$$

where we use $H_{\rm ph}$ of equation (3.7), $H_{\rm sol}$ of equation (3.8) and $H_{\rm int}^{\rm eff}$ of equation (3.21). We now wish to investigate the impact of Toda solitons on the phonon energy flux. For a particular phonon mode with a wavevector k, the associated energy flow can be calculated within the framework of Zubarev's NSOT as

$$\langle \dot{H} \rangle = {\rm Tr}[\dot{H}_k \hat{\rho}(t)] \tag{4.2}$$

where the overdot will henceforth denote a time derivative. The density matrix $\hat{\rho}(t)$ used above is formally given by NSOT as

$$\hat{\rho}(t) = Q^{-1} \exp(-B - \delta B) \tag{4.3}$$

where Q is the partition function for the phonon modes and we have defined

$$B \equiv \beta H_{\rm ph} = \beta \sum_q \hbar \Omega_q a_q^+ a_q \tag{4.4}$$

with the usual notation for $\beta = (k_{\rm B} T)^{-1}$. The small perturbation term δB is responsible for the soliton–phonon interaction and is given by

$$\delta B = \beta \int_{-\infty}^0 {\rm d}t\, {\rm e}^{\epsilon t} \sum_q \dot{H}_k(t). \tag{4.5}$$

Here, ε is a small parameter, so that time dependence is included adiabatically. The time derivative of H_k is calculated in the usual manner through the use of Heisenberg's equation of motion

$$\dot{H}_k = (\mathrm{i}\hbar)^{-1}[H_k, H_{\mathrm{tot}}] = (\mathrm{i}\hbar)^{-1}[\hbar\Omega_k a_k^+ a_k, H_{\mathrm{int}}^{\mathrm{eff}}]. \tag{4.6}$$

This is found explicitly as

$$\dot{H}_k = \sum_n \dot{H}_k(n) e_n(t) \tag{4.7}$$

where

$$\dot{H}_k(n) = -\mathrm{i}\Omega_k \frac{\chi}{b^2}\left(\alpha_k^{n^*} a_k^+ - \alpha_k^n a_k + \sum_q \alpha_k^{n^*}\alpha_q^n a_k^+ a_q - \alpha_q^{n^*}\alpha_k^n a_q^+ a_k - \alpha_q^n \alpha_k^n a_q a_k + \alpha_q^{n^*}\alpha_k^{n^*} a_q^+ a_k^+\right) \tag{4.8}$$

and

$$e_n(t) = \exp[b(\beta_{n-1} - \beta_n)] - 1. \tag{4.9}$$

In the continuum approximation [11] the latter coefficient becomes

$$e_n(t) = \sinh^2(\mu)\,\mathrm{sech}^2[(\mu/R_0)(nR_0 - x_0 - vt)]. \tag{4.10}$$

Making use of equation (4.9) in [11] and employing the results presented in this section gives the average energy flow for the k-mode as

$$\langle \dot{H}_\kappa \rangle = \langle \dot{H}_\kappa \rangle_0 - \sum_n \sum_l \sum_k \int_{-\infty}^{0} \mathrm{d}t\, \mathrm{e}^{\varepsilon t} \int_0^1 \mathrm{d}\lambda\, \langle \mathrm{e}^{\lambda B} \dot{H}_\kappa(n,0) \mathrm{e}^{-\lambda B} \dot{H}_\kappa(l,t) \rangle_0 \langle e_n(0) e_l(t) \rangle_{\mathrm{cl}}. \tag{4.11}$$

Here, $\langle\cdots\rangle_0$ denotes taking the expectation value with respect to the equilibrium statistical operator $\hat{\rho}_0$ where

$$\hat{\rho}_0 \equiv \mathrm{e}^{-B}/\mathrm{Tr}\,\mathrm{e}^{-B}. \tag{4.12}$$

In equation (4.11), the symbol $\langle\cdots\rangle_{\mathrm{cl}}$ is the classical time-dependent force–force correlation function defined following Mertens and Büttner [6] and is expressed as

$$\langle e_n(0) e_l(t) \rangle_{\mathrm{cl}} = \frac{1}{D} \int_{-\infty}^{+\infty} \mathrm{d}x_0 \int \mathrm{d}v \left(\frac{v}{c}\right)^4 \mu^4 \exp\left(-\frac{E_0 + \frac{1}{2}M^* v^2}{k_B T}\right) \times \mathrm{sech}^2\left(\frac{\mu}{R_0}(nR_0 - x_0)\right) \mathrm{sech}^2\left(\frac{\mu}{R_0}(lR_0 - x_0 - vt)\right) \tag{4.13}$$

where D is the classical partition function of the anharmonic Toda chain. Since μ is velocity-dependent through equation (2.6), a closed-form solution of the integral in equation (4.13) is not possible [6]. In order to provide a semiquantitative estimate of the expression in equation (4.13), we introduce an average solitonic parameter $\bar{\mu}$ in subsequent calculations.

First of all, when evaluating the λ integral in equation (4.11) we use retarded Green functions of the type

$$\Gamma_{\kappa k}(t) \equiv \langle\langle a_\kappa^+(0)|\dot{H}_k(l,t)\rangle\rangle = [\theta(-t)/\mathrm{i}\hbar]\langle[a_\kappa^+, \dot{H}_k(l,t)]\rangle_0 \tag{4.14}$$

where θ is the Heaviside theta function, so that

$$\theta(-t) = \begin{cases} 1 & \text{for } t < 0 \\ 0 & \text{for } t > 0. \end{cases} \tag{4.15}$$

With these definitions, we obtain for equation (4.11)

$$\begin{aligned} \langle \dot{H}_\kappa \rangle = & -\sum_n \sum_l \sum_k \int_{-\infty}^{+\infty} \mathrm{d}t \, \mathrm{e}^{\varepsilon t} \frac{\chi}{b^2} \Bigg[-\alpha_\kappa^{n^*} \langle\langle a_\kappa^+ | \dot{H}_k(l,t)\rangle\rangle - \alpha_\kappa^n \langle\langle a_\kappa | \dot{H}_\kappa(l,t)\rangle\rangle \\ & - \Omega_\kappa \sum_q \Bigg(\frac{\alpha_\kappa^{n^*}\alpha_q^n}{\Omega_\kappa - \Omega_q} \langle\langle a_\kappa^+ a_q | \dot{H}_k(l,t)\rangle\rangle + \frac{\alpha_\kappa^n \alpha_q^{n^*}}{\Omega_\kappa - \Omega_q} \langle\langle a_q^+ a_\kappa | \dot{H}_\kappa(l,t)\rangle\rangle \\ & + \frac{\alpha_\kappa^n \alpha_q^n}{\Omega_\kappa + \Omega_q} \langle\langle a_q a_\kappa | \dot{H}_k(l,t)\rangle\rangle + \frac{\alpha_\kappa^{n^*}\alpha_q^{n^*}}{\Omega_\kappa + \Omega_q} \langle\langle a_q^+ a_\kappa^+ | \dot{H}_k(l,t)\rangle\rangle \Bigg) \Bigg] \langle e_n(0) e_l(t)\rangle_{\mathrm{cl}}. \end{aligned} \tag{4.16}$$

In this calculation we made use of the fact that $\langle \dot{H}_k \rangle_0 = 0$ since $\mathrm{Tr}(\hat{\rho}_0 \dot{H}_k) \equiv 0$. Next, we define Fourier transforms of Green functions as

$$\Gamma_{\kappa k}(t) \equiv \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{e}^{-\mathrm{i}\omega t} \Gamma_{\kappa k}(\omega) \tag{4.17}$$

where

$$\Gamma_{\kappa k}(\omega) = \langle\langle a_\kappa^+ | a_k \rangle\rangle_\omega. \tag{4.18}$$

Consequently, the following auxiliary expressions are obtained

$$\langle\langle a_\kappa^+ | a_k \rangle\rangle_\omega = -\delta_{\kappa k}/\hbar(\omega + \Omega_\kappa) \tag{4.19}$$

$$\langle\langle a_\kappa | a_k^+ \rangle\rangle_\omega = -\delta_{\kappa k}/\hbar(\omega - \Omega_\kappa) \tag{4.20}$$

$$\langle\langle a_\kappa^+ a_q | a_k^+ a_{q'} \rangle\rangle_\omega = \frac{\delta_{qk}\delta_{\kappa q'}}{\hbar(\omega - \Omega_q + \Omega_\kappa)} (\bar{N}_\kappa - \bar{N}_q) \tag{4.21}$$

$$\langle\langle a_q a_\kappa | a_k^+ a_{q'}^+ \rangle\rangle_\omega = \frac{\delta_{\kappa q'}\delta_{qk} + \delta_{\kappa k}\delta_{qq'}}{\hbar[\omega - (\Omega_\kappa + \Omega_q)]} (\bar{N}_q + \bar{N}_\kappa + 1) \tag{4.22}$$

and

$$\langle\langle a_q^+ a_\kappa^+ | a_k a_{q'} \rangle\rangle_\omega = -\frac{\delta_{qk}\delta_{\kappa q'} + \delta_{qq'}\delta_{\kappa k}}{\hbar[\omega + (\Omega_\kappa + \Omega_q)]} (\bar{N}_q + \bar{N}_\kappa + 1) \tag{4.23}$$

where we take the mean occupation number for phonons in the usual form

$$\bar{N}_k = [\exp(\beta\hbar\Omega_k) - 1]^{-1}. \tag{4.24}$$

In order to be able to evaluate explicitly the effect of the classical soliton dynamics on the quantum degrees of freedom, we make the continuum approximation in equation (4.16) by replacing summations with integrations according to

$$\sum_n \sum_l \to \frac{1}{R_0^2} \int_{-\infty}^{+\infty} \mathrm{d}x \int_{-\infty}^{+\infty} \mathrm{d}x'. \tag{4.25}$$

Noting that

$$\alpha_q^n = \alpha_q \exp(\mathrm{i}qnR_0) \to \alpha_q \exp(\mathrm{i}qx) \tag{4.26}$$

we arrive at a number of integrals that can be carried out analytically. For example, taking the term in equation (4.22), we find

$$\frac{1}{R_0} \int_{-\infty}^{+\infty} \mathrm{d}x \, \frac{\exp[\mathrm{i}x(k+q)]}{\cosh^2[(\mu/R_0)(x-x_0)]} = \frac{\pi R_0}{\mu^2}(k+q) \frac{\exp[\mathrm{i}x_0(k+q)]}{\sinh[(\pi R_0/\mu^2)(k+q)]}. \tag{4.27}$$

Calculations involving the remaining terms present in equation (4.16) are quite analogous and we shall not present their details here for the sake of brevity. The next step is to perform the requisite integration with respect to the position coordinate x_0 of the centre of a Toda soliton. In the same example as before, i.e. for equation (4.22), we obtain

$$\frac{1}{NR_0} \int_{-\infty}^{+\infty} \mathrm{d}x_0 \, \exp[\mathrm{i}x_0(\kappa + q - k - q')] = \delta_{\kappa+q,k+q'}. \tag{4.28}$$

This then makes the subsequent integration with respect to time t very simple indeed

$$\int_{-\infty}^{+\infty} \mathrm{d}t \, \exp[-\mathrm{i}(\omega + \kappa + q)t] = \frac{2\pi}{|\kappa + q|} \delta \left(v + \frac{\omega}{\kappa + q} \right). \tag{4.29}$$

Once again, we wish to emphasize that both the solitonic parameter μ and the effective mass of a TS depend on the propagation velocity v. Thus, in view of the result in equation (4.29) and the expression (4.13), the velocity averaging procedure simply replaces v by $|\omega/(\kappa+q)|$. Hence, the integrand in equation (4.13), denoted for convenience as $f[v; \mu(v); M^*(v)]$, exhibits a sharp resonant behaviour as a result of scattering. We may, therefore, write

$$\int \mathrm{d}v \, f[v; \mu(v); M^*(v)] = f\left[\left(\frac{\omega}{\kappa+q} \right); \mu \left(\frac{\omega}{\kappa+q} \right); M^* \left(\frac{\omega}{\kappa+q} \right) \right] = F \left(\frac{\omega}{\kappa+q} \right). \tag{4.30}$$

Finally, the inverse Fourier transform of the Green function above leads to a Cauchy-type integral

$$\frac{1}{2\pi \mathrm{i}} \int_{-\infty}^{+\infty} \frac{F(\omega/(\kappa+q))}{\omega - (\Omega_\kappa + \Omega_q)} \, \mathrm{d}\omega = F \left(\frac{\Omega_k + \Omega_q}{\kappa + q} \right). \tag{4.31}$$

We, therefore, conclude that TS are characterized by an 'average' solitonic parameter μ_0, which satisfies the implicit formula

$$c \sinh(\mu_0)/\mu_0 = (\Omega_k + \Omega_q)/(k+q) \tag{4.32}$$

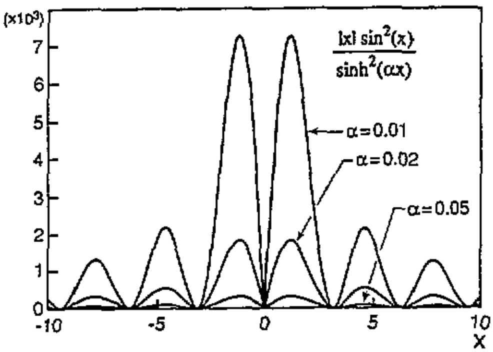

Figure 1. Plot of the k dependence of the summands in the first term of equation (4.36).

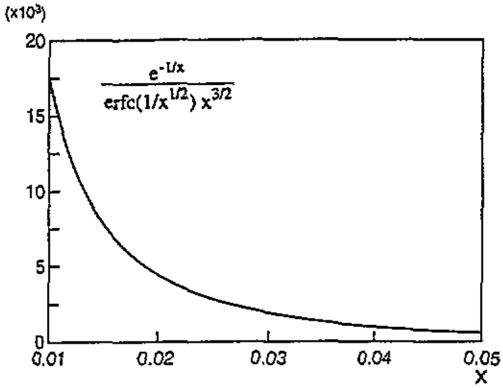

Figure 2. Temperature dependence of the thermal conduction coefficient K of equation (4.42).

and contribute resonantly to the process of energy transfer.

Carrying out these calculations for the remaining terms in equation (4.16) we find the following expression for the energy flow of a single mode κ

$$\langle \dot{H}_\kappa \rangle = \frac{8\pi^3 R_0^3 \chi^2 \mu_0^4}{DMb^2} \exp[-\beta(E_0 + \tfrac{1}{2}M_0^* c^2)] \frac{|\kappa| \sin^2(\frac{1}{2}\kappa R_0)}{\sinh^2(\pi R_0 \kappa / 2\mu_0)} + \frac{132\pi^3 R_0^3 \hbar \chi^2 \mu_0^4}{DNM_c^2} \times \exp[-\beta(E_0 + \tfrac{1}{2}M_0^* c^2)] \sum_q (\bar{N}_\kappa + \bar{N}_q + 1) \frac{|\kappa|}{q} \frac{\sin^2(\frac{1}{2}\kappa R_0) \sin^2(\frac{1}{2} q R_0)}{\sinh^2[\pi R_0(\kappa + q)/2\mu_0]} \tag{4.33}$$

where $M_0^* = 2M\mu_0$ and the normalization factor is given by

$$D = 2NR_0(\pi/2M_0^*\beta)^{1/2} \exp(-E_0\beta)\{1 - \Phi[(M_0^*\beta/2)^{1/2}c]\}. \tag{4.34}$$

Here, Φ is the error function defined in the usual way as

$$\Phi(\sigma) \equiv \int_0^\sigma \mathrm{d}Y \exp(-Y^2). \tag{4.35}$$

In order to find the total energy flow, contributions of the type in equation (4.33) must be summed over all wavenumbers κ. This yields

$$\langle \dot{H} \rangle = \frac{1}{N}\alpha \sum_\kappa \frac{|\kappa| \sin^2(\frac{1}{2}\kappa R_0)}{\sinh^2(\pi R_0 \kappa / 2\mu_0)} + \frac{1}{N^2}\gamma \sum_{\kappa, q} \frac{|\kappa|}{q} (\bar{N}_\kappa + \bar{N}_q + 1) \frac{\sin^2(\frac{1}{2}\kappa R_0) \sin^2(\frac{1}{2} q R_0)}{\sinh^2[\pi R_0(\kappa + q)/2\mu_0]} \tag{4.36}$$

where the following symbols have been used

$$\alpha = \frac{4\pi^3 R_0^2 \chi^2 \mu_0^4}{\{1 - \Phi[(M_0^*\beta/2)c]\} b^2 M} \left(\frac{2M_0^*\beta}{\pi}\right)^{1/2} \exp\left(-\frac{\beta}{2} M_0^* c^2\right) \tag{4.37}$$

and

$$\gamma = (33\hbar b^2 R_0 / Mc)\alpha. \tag{4.38}$$

It is not difficult to see that the first sum in equation (4.36) dominates the picture. In figure 1 we have shown how the various κ-modes contribute to it for a range of values of (π/μ_0). The function has a damped oscillatory profile with its peak values diminishing successively.

It would certainly be instructive to make numerical estimates of the calculated effect. At present the only data available for Toda solitons in actual physical systems are those pertaining to DNA. In this case, Muto *et al* [16, 17] provided the following estimates of the model parameters:

$$\chi = 31.7\ \mathrm{N\ m^{-1}} \qquad b = 6.18 \times 10^{10}\ \mathrm{m^{-1}} \qquad c = 1.69 \times 10^{3}\ \mathrm{m\ s^{-1}}$$
$$R_0 = 3 \times 10^{-10}\ \mathrm{m} \qquad M \simeq 10^{-25}\ \mathrm{kg}. \tag{4.39}$$

This set of values leads to the relationship: $\gamma \simeq 2 \times 10^{-2}\alpha$. As hinted at earlier, the contribution due to the two-phonon interaction in equation (4.36) is negligible compared to the first term reflecting the TS–phonon coupling.

A further approximation we wish to make is to ignore the κ dependence of the effective solitonic parameter μ_0 in equation (4.32). This is, in fact, exactly satisfied in the linear regime of the phonon dispersion relation. We then make a transition to the continuum limit and, performing the integration over κ, produce the following relatively simple result

$$\langle \dot{H} \rangle \simeq \frac{24\sqrt{2}}{\pi^{5/2}}\xi(3) R_0 \left(\frac{\chi}{b}\right)^2 \frac{\mu_0^{9/2}}{(Mk_\mathrm{B}T)^{1/2}} \frac{\exp(-M_0^* c^2/2k_\mathrm{B}T)}{1 - \Phi[(M_0^*/2k_\mathrm{B}T)^{1/2}c]}. \tag{4.40}$$

Our working assumption now is that the energy flow along the molecular chain brings about a temperature gradient with a smooth profile along the chain. For a very long chain, the temperature difference between neighbouring sites is negligibly small and we can write the energy flux due to soliton propagation as

$$\Phi \equiv \langle \dot{H} \rangle / R_0^2 = KT/R_0 \tag{4.41}$$

where K ($\mathrm{W^{-1}\ K^{-1}}$) is the thermal conduction coefficient given explicitly as

$$K = \frac{24\sqrt{2}}{\pi^{5/2}}\xi(3) \left(\frac{\chi}{b}\right)^2 \frac{\mu_0^{9/2}}{(k_\mathrm{B}M)^{1/2}} \frac{\exp(-M_0^* c^2/2k_\mathrm{B}T)}{1 - \Phi[(M_0^*/2k_\mathrm{B}T)^{1/2}c]} T^{-3/2}. \tag{4.42}$$

This coefficient, plotted as a function of temperature, is shown in figure 2. It is a smooth function decreasing at both the low- and high-temperature limit and peaking at a characteristic temperature given by $T_\mathrm{M} = 2M_0^* c^2/3k_\mathrm{B}$. This type of behaviour can be readily verified by experiment and we encourage experimentalists to undertake the required measurements for monatomic anharmonic lattices. Based on our analysis, it is clear that the narrower the TS, the larger the value of T_M and, conversely, broad solitons would lead to low values of T_M.

5. Discussion and conclusions

The main objective of this paper has been to estimate the contribution to heat conductivity due to the interactions between Toda solitons and lattice phonons in non-linear monatomic chains governed by perturbed Toda potentials in the absence of impurities. We have demonstrated that, without a doubt, interactions between localized modes (solitons) and phonons will be manifested through a finite contribution to the heat conduction coefficient. This contribution will have a specific dependence on temperature, as has been shown in detail in section 4. In this connection, recent numerical simulations [5] demonstrated that, in perfect non-linear lattices that support the existence of pulse-like excitations, a number of interesting phenomena emerge. In particular, pulsed excitations create 'peaks' that propagate ballistically along the chain. Their speeds exceed the harmonic sound velocity and the profiles resemble solitary waves. It was concluded that, due to anharmonicity, initially localized modes become delocalized. This effect is responsible for the anomalous diffusion regime of the energy transport.

The main result of this paper is the thermal conduction coefficient of equation (4.42), which exhibits a pronounced maximum at a characteristic temperature T_M. In very pure crystals, e.g. NaF, a similar effect has been seen experimentally [5]. There, $T_M = 16.5$ K and the corresponding value of heat conductivity is $K = 2.4 \times 10^4$ W m^{-1} K^{-1}. It is conceivable that the mechanism responsible for this effect is closely related to the one discussed in our paper.

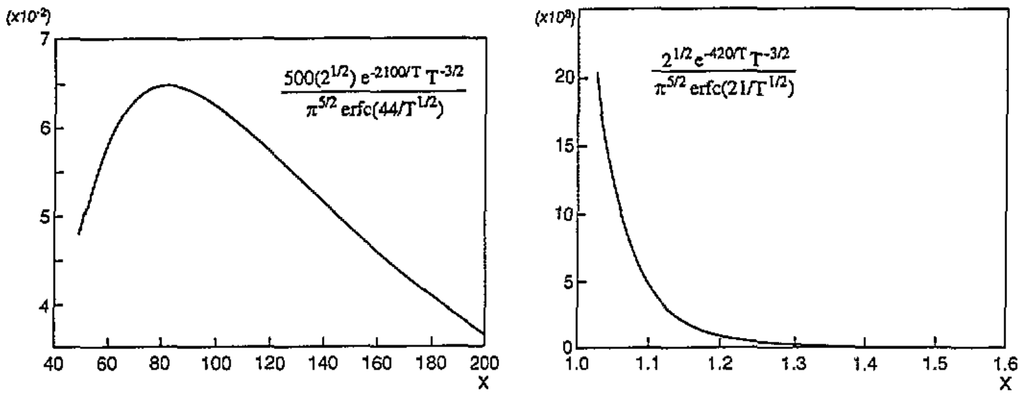

Figure 3. Plots of $K(T)$ for (*a*) $\mu_0 = 0.1$ as in equation (5.1) and (*b*) $\mu_0 = 0.02$ as in equation (5.2).

In the only case for which numerical data are available to us, i.e. DNA, we can carry the discussion even further. The model parameters given by equation (4.39) still leave one arbitrary coefficient, i.e. the solitonic parameter μ_0. Choosing two representative values of μ_0, for example, $\mu_0 = 0.1$ and $\mu_0 = 0.02$ to represent the average values for long-wavelength TS, we obtain the conduction coefficient as follows:

$$K(\mu_0 = 0.1) = \frac{5\sqrt{2} \times 10^2}{\pi^{5/2}} \frac{\exp(-2.1 \times 10^3/T)}{1 - \Phi(44T^{-1/2})} T^{-3/2} \tag{5.1}$$

and

$$K(\mu_0 = 0.02) = \frac{\sqrt{2}}{\pi^{5/2}} \frac{\exp(-420/T)}{1 - \Phi(21T^{-1/2})} T^{-3/2} \tag{5.2}$$

respectively. These expressions give the coefficient K in SI units and have been plotted in figure 3. We believe that the increase of K with decreasing temperature reflects the fact that the average number of TS, N_S, grows with T. For example, Muto *et al* [16] report that $N_S \sim T^{1/2}$, while Mertens and Büttner [6] predict a linear dependence on temperature $N_S \sim T$. Eventually, however, increasing the temperature must lead to a saturation of the lattice with Toda solitons and N_S must reach its asymptotic limit. At the same time soliton collisions and their scattering of the phonon gas must increase with temperature. This would result in an effective decrease of the mean free path. It is, therefore, clear that the two tendencies are in direct competition. Soliton production and scattering effects lead to a balance that is reflected in the form of $K(T)$ characterized by: growth, peak and asymptotic decrease.

It has been shown [19] that the anharmonic interaction between phonons leads to three-phonon scattering processes, which are referred to as Umklapp processes. This phenomenon shows an exponential decrease of conductivity as a function of temperature. The only difference in comparison with our approach is that, instead of the Debye energy $\hbar\omega_D = k_B T_D$, we have the solitonic energy $M^*c^2/2$ in the exponential factor. It is also worth noting that in our mechanism the behaviour of $K(T)$ for higher temperatures satisfies the relationship

$$K(T) \sim T^{-3/2} \tag{5.3}$$

while on the basis of pure phonon–phonon interactions [19] it has the form

$$K(T) \sim T^{-1} \tag{5.4}$$

since the phonon's mean free path is $\bar{l} \sim T^{-1}$, so that in the classical expression

$$K = \tfrac{1}{3} C_T \bar{v} \bar{l} \tag{5.5}$$

only $\bar{l}$ depends on temperature. Here, C_T is the specific heat and $\bar{v}$ is the average drift velocity of elastic waves. In our mechanism, however, $\bar{l}$ decreases with T faster than that since the velocities of TS increase and the collisions with phonons become more frequent.

Acknowledgments

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References

[1] Peierls R E 1961 *Theoretical Physics in the Twentieth Century* ed M Fiera and V F Weisskopf (New York: Wiley)
[2] Joseph D D and Preziosi L 1989 *Rev. Mod. Phys.* **61** 41
[3] Toda M 1979 *Phys. Scr.* **20** 424
[4] Payton D N, Rich M and Visscher W M 1967 *Phys. Rev.* **160** 706
[5] Jackson H E, Walker C T and McNelly T F 1970 *Phys. Rev. Lett.* **25** 16
[6] Mertens F G and Büttner H 1986 *Solitons* ed S E Trullinger, V E Zakharov and V L Pokrovsky (Amsterdam: Elsevier) p 723
[7] Hénon M 1974 *Phys. Rev.* B **39** 1921
[8] Sutherland B 1978 *Rocky Mount. J. Math.* **8** 413
[9] Mokross F and Büttner H 1983 *J. Phys. C: Solid State Phys.* **16** 4539
[10] Zubarev D N 1971 *Non-Equilibrium Statistical Thermodynamics* (Moscow: Nauka) in Russian
[11] Satarić M V and Tuszyński J A 1991 *Phys. Rev.* B **43** 8450
[12] Cassati G, Ford J, Vivaldi F and Visscher W M 1984 *Phys. Rev. Lett.* **52** 1861
[13] Davydov A S 1991 *Solitons in Molecular Systems* 2nd edn (Amsterdam: Kluwer)
[14] Toda M 1967 *J. Phys. Soc. Japan* **22** 431
[15] Satarić M V, Žakula R B, Zeković S and Tuszyński J A 1993 *Phys. Scr.* **47** 315
[16] Muto V, Scott A C and Christiansen P L 1990 *Physica* D **44** 75
[17] Satarić M V, Tuszyński J A, Žakula R B and Ivić Z 1992 *Surf. Sci.* **260** 370
[18] Bourbonnais R and Maynard R 1990 *Phys. Rev. Lett.* **64** 1397
[19] Vandersande J W and Wood C 1986 *Contemp. Phys.* **27** 117