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Transverse intrinsic localized modes in monatomic chain and in graphene

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ABSTRACT

In this paper an analytical and numerical study of anharmonic vibrations of monatomic chain and graphene in transverse (perpendicular) with respect to the chain/plane direction is presented. Due to the lack of odd anharmonicities and presence of hard quartic anharmonicity for displacements in this direction, there may exist localized anharmonic transverse modes with the frequencies above the spectrum of the corresponding phonons. Although these frequencies are in resonance with longitudinal (chain) or in-plane (graphene) phonons, the modes can decay only due to a weak anharmonic process. Therefore the lifetime of these vibrations may be very long. E.g. in the chain, according to our theoretical and numerical calculations it may exceed 10^{10} periods. We call these vibrations as transverse intrinsic localized modes.

1. Introduction

It is a well-known fact that point defects in crystals may cause an appearance of spatially localized vibrations, called local modes (see, e.g. [1]). The frequency of such modes lies outside the phonon spectrum, which prevents the spreading of the vibrations to the bulk. Besides, resonant or pseudolocal modes with the frequencies inside the phonon spectrum may also exist. They appear when the frequency of the leading vibration associated with the defect gets to a region of small density of states (DOS) of phonons. Unlike local modes, which are stable in harmonic approximation, these modes can live only a finite time due to the emission of resonant phonons. However, because of the small DOS of resonant phonons the interaction of the latter with pseudolocal mode is weak, due to that the lifetime of the mode becomes long. A well-known case of long-living pseudolocal modes in 3D lattices is the one by the defect of large mass [1].

Spatially localized modes may exist also in perfect nonlinear lattices. Such modes in chains with cubic and quartic anharmonicity were first described by A.M. Kosevich and A.S. Kovalev [2]. They have found that for sufficiently strong quartic anharmonicity there exist vibrational states localized in the space and periodic in time; the frequency of these vibrations exceeds the maximum frequency of phonons. The authors [2] restricted their consideration with large-size vibrations and the frequency close to the top of the phonon spectrum. Small size localized vibrations in anharmonic lattices were introduced by Dolgov [3] and then by A.J. Sievers and S. Takeno [4] and were called “intrinsic localized modes” (ILMs).

In the numerical studies of ILMs different two-body potentials (Lennard–Jones, Born–Mayer–Coulomb, Toda, and Morse potentials and their combinations) have been used (see, e.g. [5–7]). All these potentials have strong odd anharmonicities and show a strong softening with the increasing of the vibrational amplitude. The ILMs found in these simulations always drop down from optical band(s) into the phonon gap, if there is any. In this connection see Ref. [8], where gap ILMs in NaI were calculated without taking into account long-range interactions and Ref. [9], where the calculations of ILMs in NaI were made taking these interactions into account.

Usually in crystal lattices odd anharmonicities are strong and pair potentials show a strong softening with the increase of vibrational amplitude. Therefore, the dropping down of the frequency of ILMs from optical bands is quite common in 3D lattices. Still, as it was shown in Refs. [10–13], in some crystals odd anharmonicities are reduced due to multiparticle or covalent interactions. Examples have been given with germanium [10], diamond [11], metallic Ni, Nb [12], iron [13] and copper [11]; in all these crystals ILMs with frequencies above the top of the phonon band were found in numerical simulations.

However, there are systems in which the odd anharmonicities disappear due to symmetry arguments; at the same time, the quartic anharmonicity is nonzero and it is hard (positive). The examples of such systems are given by linear atomic chains

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and planar atomic structures (e.g. graphene); in these systems odd anharmonicities disappear for vibrations in the transverse (out-of-chain and out-of-plane) direction. Therefore, one can expect that in these systems there can exist transverse anharmonic local modes with the frequencies above the maximum frequency of the corresponding phonons. The latter frequencies are usually smaller than the maximum frequency of longitudinal/in-plane phonons. These modes fall in resonance with these phonons and can decay. However, unlike pseudolocal modes and like local modes the interaction causing the decay of these modes is anharmonic. Therefore we call them as transverse ILMs (TILMs). The anharmonic interaction of TILMs with small vibrational amplitudes of atoms is very weak. Hence, one can expect that the lifetime of such TILM may be rather long. Below we will consider TILMs in a monatomic chain and in graphene, both analytically and numerically. Our considerations confirm the aforesaid expectation.

2. Anharmonic chain

First we consider the anharmonic monatomic chain and examine the vibrations of its atoms in transverse (y) directions. We suppose that the potential energy U of the chain is given by the sum of pair potentials $V(R_{n,n'})$, where $R_{n,n'}$ is the distance between the atoms n and n'. The latter potentials can be expanded into the series of atomic displacements. Denoting $d=(n-n')\ a$, $x=x_n-x_{n'}$, $y=y_n-y_{n'}$, where a is the atom spacing, x_n and y_n are the longitudinal and transverse displacements of the atom number n from its equilibrium position, we get $R\equiv R_{n,n'}=\sqrt{(d+x)^2+y^2}$. As y appear as y^2, any power expansion of R will have only even powers of y. The same holds for U. This means that U indeed has no odd anharmonic terms. This is a consequence of the symmetry of the chain with respect to the change of the sign of y.

Note one more property of the chain: the term in the expansion of R, quadratic with respect to y, has the same numerical factor as the term linear with respect to x. The same holds also for an arbitrary power of R. In the equilibrium state all linear terms with respect to the coordinates x in the potential energy U are cancelled. Therefore, all quadratic terms with respect to y are also cancelled, i.e. the frequencies of transverse vibrations in the pair potential approximation tend to zero. As a result long-range fluctuations can be created with little energy cost and since they increase the entropy they are favored. This leads to the instability of the chain with respect to small transverse distortions (see in this connection the Mermin–Wagner theorem [14]).

To get the chain stable one needs to stretch it [15]. In this case the atom spacing a is replaced by $a+s$, where s is stretching. Then the terms in U linear with respect to x and y^2 are not cancelled any more. Therefore, the elastic springs for transverse vibrations are also nonzero and positive. This results in the appearance of transverse phonons with finite, although small for small stretching maximum frequency ω_{tm}. As these phonons do not have any cubic anharmonicity, but have nonzero positive quartic anharmonicity, low-frequency TILMs with the frequency above the spectrum of transverse phonons should exist here.

Let us consider the TILM in a monatomic chain with the Morse pair potential

$$V=D(1-e^{\alpha(a-r)})^2. \tag{1}$$

Here D is the energy of dissociation, α is the parameter. We are using dimensionless coordinates with the units corresponding to $a=1$ and the value $\alpha=4$ of the Morse pair potentials of atoms in monatomic metals. For this potential only nearest-neighbor interactions are essential and only these potentials will be taken into account here. We also take for the mass units the mass of the atoms of the chain ($M=1$). The dissociation energy is chosen so that the unit frequency will correspond to the maximum frequency of longitudinal phonons. In this case the potential energy of the stretched lattice is the sum of the following pair potentials (up to a constant term):

$$V=\left(1-e^{-4(r-1)}\right)^2\Big/128-x\left(1-e^{-4s}\right)e^{-4s}\Big/16, \tag{2}$$

where $r=\sqrt{(x+1+s)^2+y^2}$. The last term in Eq. (2) accounts for the effect of the stretching force of the chain in x direction – it changes the equilibrium distance of the atoms from $r=1$ to $r=1+s$. Let us expand the potential into the series of x and y and take into account up to the second-order terms with respect to x and forth-order terms with respect to y. We get (up to a constant)

$$V(x,y)\approx\frac{\nu_1}{8}x^2+\frac{\nu_2}{8}sy^2+\frac{\nu_3}{8}xy^2+\frac{\nu_4}{32}y^4, \tag{3}$$

where ν_i are dependent on stretching s parameters. In the small s limit $\nu_i\approx 1$. If $s=0.05$ then $\nu_1\approx 0.522$, $\nu_2\approx 0.707$, $\nu_3\approx 0.463$, $\nu_4\approx 0.441$.

The pair potential of the longitudinal vibrations alone is given by the first term in the right-hand side of Eq. (3). Vibrational frequencies of corresponding phonons equal [1]

$$\omega_k=\sqrt{\nu_1\,(1-\cos(k))\,/2}. \tag{4}$$

The maximum frequency of longitudinal phonons corresponds to $k=-\pi$ and equals $\omega_{lm}=\sqrt{\nu_1}$. The transverse vibrations alone are described by the pair potential

$$V(0,y)=\frac{\nu_2 s}{8}\,y^2+\frac{\nu_4}{32}\,y^4. \tag{5}$$

In harmonic approximation ($\nu_4=0$) the frequencies of corresponding phonons are given by Eq. (4) with $\nu_2 s$ instead on ν_1. The positive quartic anharmonicity in Eq. (5) leads to appearance of the anharmonic modes [2] (called here as TILMs) with the frequencies $\omega_0=\omega_{tm}\sqrt{1+\varepsilon^2/4}$ above the maximum frequency of transverse phonons $\omega_{tm}=\sqrt{\nu_2 s}$ and with the displacements

$$y_n(t)\approx(-1)^n A_0\,\cosh^{-1}(\varepsilon n)\cos(\omega_0 t)\,. \tag{6}$$

Here A_0 is the amplitude of the central atom,

$$\varepsilon=\sqrt{3\nu_4}\,A_0/\omega_{tm} \tag{7}$$

is the reversed size of the TILM (we use the discrete analog of the derived in Ref. [2] equation (47) for the difference in the displacements of two neighboring atoms $\chi(x)$). These modes interact with longitudinal phonons and, therefore, they decay. To describe this decay we consider the longitudinal vibrations of atoms in the presence of the TILM. Taking into account Eq. (6) we replace y by $y(t)$ in Eq. (3) and get the following pair potential for this motion:

$$V(x,t)\approx\frac{\nu_1}{8}x^2+\frac{\nu_3}{16}xy^2(0)+\frac{\nu_3}{16}xy^2(0)\cos(2\omega_0 t). \tag{8}$$

The first term in the right-hand side of this equation gives the potential energy of the longitudinal vibrations alone in harmonic approximation. The second and the third terms describe the anharmonic interaction of these and transverse vibrations. At that the second term stands for a small local compression, while the third term describes the force with the frequency $2\omega_0$ periodically changing in time. For all longitudinal phonons, except those with the resonant frequency $\omega_k=2\omega_0$, this force causes forced vibrations of atoms with the frequency $2\omega_0$. The resonant term causes the increase of the energy of phonons in time. From energy conservation law it follows that this energy comes from the TILM, i.e. the TILM decays.