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Intrinsic Localized Anharmonic Modes at Surfaces and Edges

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Summary

Intrinsic localized anharmonic modes (ILMs) are vibrational states of a crystal lattice that involve only a small number of lattice sites similar to defect modes. However, the localization of their displacement pattern is not due to any inhomogeneity of the lattice, but due to the nonlinearity of the interaction potential (see Refs. [1-4] for pioneering work on this subject). In our presentation, we have reported about ILMs that occur at surfaces or edges of crystal lattices. In the case of two- and three-dimensional crystals, the displacement patterns of surface ILMs are not only localized in the direction normal to the surface, but also in the direction(s) along the surface. Likewise, the ILMs at edges of a three-dimensional crystal are localized in the direction along the edge as well as in the plane perpendicular to the edge.
The material of our presentation is largely contained in three publications [5-7].
At first, simple cubic lattices have been considered with one degree of freedom per lattice site. This scalar degree of freedom need not be a displacement component of lattice particles, but may have a different physical meaning like, for example, a rotation angle in a molecular crystal. Introducing anharmonic nearest-neighbour interactions between the lattice sites, surface ILMs have been found for 1-, 2-, and 3-dimensional simple-cubic lattices with a cubic axis being normal to the surfaces. Their stability has been investigated by molecular dynamics and in many cases by a semi-numerical linear stability analysis which is described in [5]. Some of the modes have been found to be stable, others started to move along the surface, and an instability associated with radiation of energy into the bulk has been found in the presence of cubic anharmonicity.
The search for ILMs has been extended to realistic 3-dimensional crystals with 3-dimensional displacement vectors and realistic interaction potentials [6]. Intrinsic localized edge modes have been found for an alkali halide crystal

(NaI) with Born-Mayer potentials and the Coulomb potential between up to second-nearest neighbours. The edge was bounded by two cubic planes of the crystal. Molecular dynamics simulations did not show any sign of an instability of the edge ILM.
A system on which anharmonic effects have already been studied experimentally [8,9] is the Si(111):H adlayer system. Using the rigid-substrate approximation and *ab initio* data for the anharmonic on-site potential [10,11] of the hydrogen atoms, ILM solutions have been found and verified by molecular dynamics.

The coefficients in the Nonlinear Schrödinger equation for guided lattice modes

The surface and edge ILMs in the realistic systems with 3-component displacement vectors have been found in the following way. At first, the frequency spectrum of the harmonic modes is determined. The displacement vectors $\vec{u}$ associated with a linear phonon mode with wavevector $\vec{q}$ and branch index j may be written in the form

$$u_\alpha \begin{pmatrix} l \\ \kappa \end{pmatrix} = \tilde{w}_\alpha(\kappa|\vec{q}j) e^{i(\vec{q}\cdot\vec{R}(l)-\omega_0 t)}\, \psi \; + \; c.c. \tag{1}$$

Here, $\alpha = x, y, z$ is a Cartesian index, l labels the elementary cell of the underlying periodic lattice structure, $\vec{R}(l)$ is the position of the elementary cell and κ is the sublattice index, ω_0 is the harmonic frequency and ψ the amplitude of the mode. The vectors $\vec{\tilde{w}}$ are related to the eigenvectors $\vec{e}$ of the dynamical matrix [12] via

$$\tilde{w}_\alpha(\kappa|\vec{q}j) = [M_\kappa]^{-1/2} e_\alpha(\kappa|\vec{q}j). \tag{2}$$

Here, M_κ is the mass of an atom of sublattice κ, and we have normalized the eigenvectors in the usual way:

$$\sum_{\kappa\alpha} |e_\alpha(\kappa|\vec{q}j)|^2 = 1. \tag{3}$$

Only those phonon modes are considered which either correspond to an absolute extremum of the dispersion relation or which are limiting a gap.
Small spatial and temporal variations of the amplitude ψ of such a mode due to dispersion and nonlinearity are governed by the nonlinear Schrödinger

equation (NLS)

$$i\frac{\partial}{\partial t}\psi = \mathcal{K}_2\Delta\psi + \mathcal{K}_4|\psi|^2\psi. \tag{4}$$

In the case of edge modes, this is the 1-dimensional NLS, whereas for modes in an adsorbate layer and surface modes of a three-dimensional crystal, it is the 2-dimensional NLS.

The complex amplitude ψ is now treated as a continuous function of slow spatial coordinates and of time, and Δ is the Laplace operator in one or two dimensions. (The high symmetry of our systems causes the second spatial derivatives to occur in the form of the Laplacian.) The coefficient $\mathcal{K}_2$ is then simply given by

$$\mathcal{K}_2 = -\frac{1}{2}\frac{\partial^2}{\partial q^2}\omega_0(\vec{q}j). \tag{5}$$

Here, $\vec{q}$ is the wavevector and j the branch index of the carrier mode. As the frequency of this mode is an extremum of the phonon dispersion relation or limits a gap, the first derivatives of its frequency with respect to components of the wavevector vanish and consequently, terms proportional to first spatial derivatives do not occur in the NLS.

The coefficient $\mathcal{K}_4$ of the effective third-order nonlinearity has been calculated starting from the equations of motion for the displacement vectors $\vec{u}$ up to fourth order in the components of these vectors:

$$\begin{aligned} M_\kappa \ddot{u}_\alpha \begin{pmatrix} l \\ \kappa \end{pmatrix} &= \sum_{l'\kappa'\beta} \phi^{(2)}_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\beta \begin{pmatrix} l' \\ \kappa' \end{pmatrix} + \\ &+\frac{1}{2}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\mu} \phi^{(3)}_{\alpha\beta\mu} \begin{pmatrix} l & l' & l'' \\ \kappa & \kappa' & \kappa'' \end{pmatrix} u_\beta \begin{pmatrix} l' \\ \kappa' \end{pmatrix} u_\mu \begin{pmatrix} l'' \\ \kappa'' \end{pmatrix} + \\ +\frac{1}{6}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\mu}\sum_{l'''\kappa'''\nu} &\phi^{(4)}_{\alpha\beta\mu\nu} \begin{pmatrix} l & l' & l'' & l''' \\ \kappa & \kappa' & \kappa'' & \kappa''' \end{pmatrix} u_\beta \begin{pmatrix} l' \\ \kappa' \end{pmatrix} u_\mu \begin{pmatrix} l'' \\ \kappa'' \end{pmatrix} u_\nu \begin{pmatrix} l''' \\ \kappa''' \end{pmatrix}. \end{aligned} \tag{6}$$

A Poincaré expansion up to second order in the amplitude ψ yields the following nonlinear dispersion relation for the phonon mode under consideration:

$$\omega^2 = \omega_0(\omega_0 + 2\mathcal{K}_4|\psi|^2). \tag{7}$$

To carry out this Poincaré expansion, we write the displacement vectors $\vec{u}(t)$ as a Fourier series

$$u_\alpha \begin{pmatrix} l \\ \kappa \end{pmatrix} = \sum_n u^{(n)}_\alpha \begin{pmatrix} l \\ \kappa \end{pmatrix} e^{-in\omega t}. \tag{8}$$

Up to the desired order in ψ, we then obtain the following set of coupled equations:

$$0 = \sum \phi^{(2)}_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u^{(0)}_{\beta} \begin{pmatrix} l' \\ \kappa' \end{pmatrix} + \sum \phi^{(3)}_{\alpha\beta\nu} \begin{pmatrix} l & l' & l'' \\ \kappa & \kappa' & \kappa'' \end{pmatrix} u^{(1)}_{\beta} \begin{pmatrix} l' \\ \kappa' \end{pmatrix} u^{(-1)}_{\beta} \begin{pmatrix} l'' \\ \kappa'' \end{pmatrix}, \tag{9a}$$

$$-M_\kappa \omega^2 u^{(1)}_{\alpha} \begin{pmatrix} l \\ \kappa \end{pmatrix} = \sum \phi^{(2)}_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u^{(1)}_{\beta} \begin{pmatrix} l' \\ \kappa' \end{pmatrix}$$
$$+ \sum \phi^{(3)}_{\alpha\beta\mu} \begin{pmatrix} l & l' & l'' \\ \kappa & \kappa' & \kappa'' \end{pmatrix} \left\{ u^{(2)}_{\beta} \begin{pmatrix} l' \\ \kappa' \end{pmatrix} u^{(-1)}_{\mu} \begin{pmatrix} l'' \\ \kappa'' \end{pmatrix} + u^{(0)}_{\beta} \begin{pmatrix} l' \\ \kappa' \end{pmatrix} u^{(1)}_{\mu} \begin{pmatrix} l'' \\ \kappa'' \end{pmatrix} \right\} +$$
$$+ \frac{1}{2} \sum \phi^{(4)}_{\alpha\beta\mu\nu} \begin{pmatrix} l & l' & l'' & l''' \\ \kappa & \kappa' & \kappa'' & \kappa''' \end{pmatrix} u^{(1)}_{\beta} \begin{pmatrix} l' \\ \kappa' \end{pmatrix} u^{(-1)}_{\mu} \begin{pmatrix} l' \\ \kappa' \end{pmatrix} u^{(1)}_{\nu} \begin{pmatrix} l' \\ \kappa' \end{pmatrix}, \tag{9b}$$

$$-4M_\kappa \omega^2 u^{(2)}_{\alpha} \begin{pmatrix} l \\ \kappa \end{pmatrix} = \sum \phi^{(2)}_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u^{(2)}_{\beta} \begin{pmatrix} l' \\ \kappa' \end{pmatrix} +$$
$$+ \frac{1}{2} \sum \phi^{(3)}_{\alpha\beta\mu} \begin{pmatrix} l & l' & l'' \\ \kappa & \kappa' & \kappa'' \end{pmatrix} u^{(1)}_{\beta} \begin{pmatrix} l' \\ \kappa' \end{pmatrix} u^{(1)}_{\mu} \begin{pmatrix} l'' \\ \kappa'' \end{pmatrix}. \tag{9c}$$

The sums in the above equations run over all indices that occur twice in products. Surface or edge modes cannot give rise to macroscopic deformations because of the resisting substrate. Hence, the static displacement and the second harmonic can be written as

$$u^{(0)}_{\alpha} \begin{pmatrix} l \\ \kappa \end{pmatrix} = v^{(0)}_{\alpha}(\kappa), \tag{10a}$$

$$u^{(2)}_{\alpha} \begin{pmatrix} l \\ \kappa \end{pmatrix} = v^{(2)}_{\alpha}(\kappa) e^{2i\vec{q}\cdot\vec{R}(l)}. \tag{10b}$$

Using an expansion of $v^{(0)}_{\alpha}$ and $v^{(2)}_{\alpha}$ in terms of eigenvectors of the dynamical matrices for the wavevectors $\vec{0}$ and $2\vec{q}$, we can eliminate the static displacement and the second harmonic to obtain the above nonlinear dispersion relation with the following expression for $\mathcal{K}_4$:

$$-2\omega_0(\vec{q}j)\mathcal{K}_4(\vec{q}j) = \frac{1}{2}\tilde{V}_4(\vec{q}j, \vec{q}j, -\vec{q}j, -\vec{q}j) + \sum_j \frac{1}{\omega_0^2(0j')} |\tilde{V}_3(0j', \vec{q}j, -\vec{q}j)|^2 +$$
$$+ \frac{1}{2} \sum_{j'} \frac{1}{\omega_0^2(2\vec{q}j') - 4\omega_0^2(\vec{q}j)} |\tilde{V}_3(-2\vec{q}j', \vec{q}j, \vec{q}j)|^2. \tag{11}$$

The cubic and quartic anharmonic coupling coefficients V_3 and V_4 are defined similar to those in interacting phonon theory [13]:

$$\tilde{V}_3(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3) = \sum \phi^{(3)}_{\alpha\beta\mu} \begin{pmatrix} l & l' & l'' \\ \kappa & \kappa' & \kappa'' \end{pmatrix} \tilde{w}_\alpha(\kappa|\vec{q}_1 j_1)\tilde{w}_\beta(\kappa'|\vec{q}_2 j_2)\tilde{w}_\mu(\kappa''|\vec{q}_3 j_3)$$

$$\times N^{-1} \exp\{i[\vec{q}_1 \cdot \vec{R}(l) + \vec{q}_2 \cdot \vec{R}(l') + \vec{q}_3 \cdot \vec{R}(l'')]\}, \qquad (12a)$$

$$\tilde{V}_4(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3, \vec{q}_4 j_4) = \sum \phi^{(4)}_{\alpha\beta\mu\nu} \begin{pmatrix} l & l' & l'' & l''' \\ \kappa & \kappa' & \kappa'' & \kappa''' \end{pmatrix} \tilde{w}_\alpha(\kappa|\vec{q}_1 j_1)\tilde{w}_\beta(\kappa'|\vec{q}_2 j_2)$$

$$\times \tilde{w}_\mu(\kappa''|\vec{q}_3 j_3)\tilde{w}_\nu(\kappa'''|\vec{q}_4 j_4)$$

$$\times N^{-1} \exp\{i[\vec{q}_1 \cdot \vec{R}(l) + \vec{q}_2 \cdot \vec{R}(l') + \vec{q}_3 \cdot \vec{R}(l'') + \vec{q}_4 \cdot \vec{R}(l''')]\}. \qquad (12b)$$

The sums run again over indices that occur twice in a product, and N is the total number of elementary cells.

The relative sign of the coefficients $\mathcal{K}_2$ and $\mathcal{K}_4$ decides about whether solutions of the form of bright solitary envelopes exist. These breather solutions are used as initial data in the search algorithm for ILMs described in [6]. The breather solutions of the 2-dimensional NLS are known to be unstable [14]. However, this need not imply instability of the corresponding ILMs obtained by the search procedure in the discrete system. The absolute values of the coefficients $\mathcal{K}_2$ and $\mathcal{K}_4$ yield a rough estimate for the relation between frequency, width and maximum amplitude of an ILM. However, this estimate fails in the regime of strong nonlinearity (at large amplitudes). Here, the localization of ILMs is much stronger than predicted by the NLS, and to reach convergence of the search procedure, the width in the initial data has to be reduced.

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