Intrinsic Localized Modes in Anharmonic Crystals

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A new kind of localized mode is proposed to occur in a pure anharmonic lattice. Its localization properties are similar to those of a localized mode for a force-constant defect in a harmonic lattice. These modes, which are thermally generated like vacancies but with much smaller activation energies, may appear at cryogenic temperatures in strongly anharmonic solids such as quantum crystals as well as in conventional solids.

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The dynamics of localized modes associated with defects in impure harmonic crystals is now fairly well understood.[1] Depending on the defect mass and the bonding to the host neighbors, a spatially localized mode may occur at a frequency above or in a gap in the host vibrational spectrum. For the weak-bonding case, low-frequency resonant modes[2] may appear as well. In this paper we describe a different kind of localized mode which can occur at finite temperatures in pure crystals with sufficient anharmonicity. Although it takes more thermal energy to produce and excite these localized vibrations than to excite plane-wave anharmonic phonon modes of the crystal, these intrinsic nonlinear modes are spatially localized and can appear at any lattice site. Because of this inherent disorder, a configurational entropy term is associated with their appearance. Since the crystal free energy depends on the difference between the creation energy and the entropy contribution, these intrinsic defects (like vacancies) become possible at elevated temperatures and must be considered in a complete thermodynamic description of the anharmonic crystal properties.

Let us consider the situation for localized modes when a defect space is characterized only by a local force-constant change in the perfect harmonic lattice of N atoms. If the local force constant is much larger than that of the host, then the highest-frequency mode of the perfect crystal at ω_m is transformed into a high-frequency local mode at ω_l, whereas in the opposite limit a low-frequency resonant mode occurs at ω_r near the bottom of the phonon frequency band. For the nearest-neighbor force-constant model in both the high- and low-frequency limiting cases, the defect mode of interest can be described by an Einstein oscillator.[2,3] Hence, the mean square displacement of an atom with mass M at site n can be written generally as

$$\langle u_n^2\rangle = \zeta_n(j_{l,r})\frac{\hbar}{2M\omega_{l,r}}\coth\left[\frac{\hbar\omega_{l,r}}{2k_{\mathrm{B}}T}\right] + \sum_j \zeta_n(j)\frac{\hbar}{2M\omega(j)}\coth\left[\frac{\hbar\omega(j)}{2k_{\mathrm{B}}T}\right], \quad (1)$$

in which $j_{l,r}$ and j are indices characterizing the Einstein oscillator at frequency $\omega_{l,r}$ corresponding to the extreme local (l) or resonant (r) mode and the quasicontinuous eigenstates at frequencies $\omega(j)$ of the dynamical matrix,[1] respectively. Boltzmann's constant is denoted as k_{B} and the temperature, T. The shape function $\zeta_n(\nu)$ $(\nu = j, j_{l,r})$ is the product $\xi_n(\nu)\xi_n^*(\nu)$ of the eigenfunction $\xi_n(\nu)$ of the dynamical matrix.

There are two instructive limits which clarify the form of $\zeta_n(\nu)$, namely, the local and plane-wave cases. With the local mode centered at $n=0$, the two types of excitations in Eq. (1) are characterized by $\zeta_0(j) = O(N^{-1}) \approx 0$ and $\zeta_0(j_{l,r}) = 1$, and hence the mean squared displacement[4]

$$a^2 \equiv \frac{\hbar}{2M\omega_{l,r}}\coth\left[\frac{\hbar\omega_{l,r}}{2k_{\mathrm{B}}T}\right] \quad (2)$$

can be identified with the squared amplitude of the localized mode. In the opposite case of the perfect lattice all sites are equivalent so that $\zeta_n(j_{l,r}) = 0$ and $\zeta_n(j) = O(N^{-1})$. If we compare the root-mean-square (RMS) amplitude of the $n=0$ atom for the highest-frequency mode in the perfect crystal at ω_m with that of the local mode at ω_l, the ratio is $1/N^{1/2}$ so that the amplitude in a local mode is much larger than that of the corresponding plane-wave mode from which the local mode evolves. A similar comparison of the RMS amplitude for the plane-wave mode and that of the resonant mode both at frequency ω_r gives the same ratio, $1/N^{1/2}$. If the localization is not complete, an inhomogeneous wave still exists at some frequency $\omega \gg \omega_m$ or $\omega \ll \omega_m$ and the RMS amplitude near the defect is $O(N_d^{-1/2})$, where N_d (~ 1) is the small number of particles within the envelope of the inhomogeneous wave, and the amplitude is zero throughout the rest of the chain.[4]

In the anharmonic crystal, the frequency of a particular mode depends on the amplitude of the particles in the mode. Because the amplitude is small for a plane-wave mode but large for the localized mode, the *anharmonic contribution to a homogeneous wave solution will be much smaller than that for a localized inhomogeneous wave.* Because the degree of localization influences the mode frequency, the anharmonic dynamics leads to the existence of intrinsic localized modes. In the 1D analysis to follow, we treat only the local-mode limit since a realistic anharmonic resonant-mode spectrum requires a 3D space.[5]

Let the anharmonic potential describing the nearest-neighbor interactions for a one-dimensional (1D) chain be represented by

$$U = \frac{K_2}{2}\sum_n (u_{n+1}-u_n)^2 + \frac{K_4}{4}\sum_n (u_{n+1}-u_n)^4 , \tag{3}$$

where K_2 and K_4 are nearest-neighbor harmonic and anharmonic force constants, respectively. Paying particular attention to the localized mode due to lattice anharmonicity, we separate u_n into negative- and positive-frequency parts:

$$u_n = \alpha[\xi_n \exp(-i\omega t) + \xi_n^* \exp(i\omega t)] , \tag{4}$$

where α and ξ_n are the amplitude and the shape function, respectively. Using the rotating-wave approximation[6] to focus attention solely on terms with the factor $\exp(-i\omega t)$ and limiting our discussion to stationary localized modes for which the ξ_n's are real, we get

$$J\{2\xi_n - \xi_{n+1} - \xi_{n-1} + \lambda[(\xi_n-\xi_{n+1})^3 + (\xi_n - \xi_{n-1})^3]\} = \omega^2 \xi_n , \tag{5}$$

where

$$J = K_2/M, \quad \lambda = (3K_4/K_2)\alpha^2 . \tag{6}$$

Note that Eq. (5) with $\lambda = 0$ is the conventional eigenvalue equation for harmonic phonons with eigenfrequencies

$$\omega^2(k) = 2J[1-\cos(k)], \tag{7}$$

where $\omega_m^2 = 4J$, and ω_m is the frequency of the top of the band $\omega(k)$. The lattice constant has been set equal to unity. In the study of the effect of lattice anharmonicity, the conventional approach is to assume that the effect of anharmonicity on band phonons can be treated by a perturbative technique or a molecular-field approximation based on the self-consistent phonon theory[7] because the anharmonic modes have a relatively small amplitude. Here we are concerned with localized modes lying above the top of the band at ω_m and for such a case a nonperturbative treatment is required from the outset. The Green's-function method is invoked to rewrite Eq. (5) in terms of 1D lattice harmonic Green's functions

$$G(n,m) = \frac{1}{N}\sum_k \frac{\exp[ik(m-n)]}{\omega^2 - \omega^2(k)} = G(|m-n|) , \tag{8}$$

so that

$$\xi_n = \textstyle\sum_m G(|m-n|)V(\xi_m) , \tag{9}$$

where

$$V(\xi_n) = J\lambda[(\xi_n - \xi_{n+1})^3 + (\xi_n - \xi_{n-1})^3] . \tag{10}$$

As an illustration we consider a single-local-mode problem. Let us assume that the local mode exists at the origin, $n=0$, of the 1D lattice. The solution to Eq. (9) of interest is the odd-symmetry mode having the property $\xi_n = \xi_{-n}$ with the normalization of the shape function given by $\xi_0 = 1$. To take account of the oscillatory nature of the shape function ξ_n, we introduce a reduced shape function and reduced lattice Green's function:

$$\xi_n = (-1)^{|n|}\eta_n, \quad G(n) = [(-1)^{|n|}/\omega^2]g(n) . \tag{11}$$

By use of the identity relations[2] satisfied by lattice Green's functions, an explicit expression for Eq. (9) can be written in terms of $y = (\omega_m/\omega)^2$ as

$$\eta_n = [2/y - 1 - \eta_1]g(n) + (\lambda y/2)\sum_{m=1}^{\infty} A_{nm}(\eta_m + \eta_{m+1})^3 \tag{12}$$

for $n \geq 1$, with

$$2/y - 1 = \eta_1 + \lambda(1+\eta_1)^3 , \tag{13}$$

$$A_{nm} = g(n-m) + g(n+m) + g(n-m-1) + g(n+m+1) , \tag{14}$$

and

$$A_{1m} = [2/y - 1]A_{0m} . \tag{15}$$

Equations (12) and (13) constitute a set of nonlinear simultaneous equations. For a given value of K_4/K_2, it gives the eigenfrequency ω and the eigenfunction η_n's of the odd-symmetry mode as a function of its squared amplitude α^2. To fix the value of α^2 we use Eq. (2). Although, in principle, the defect space spanned by a single odd-symmetry localized mode extends over an infinite number of lattice sites, we now demonstrate that in certain cases this large defect space collapses to a much smaller one.

For a localized mode lying far above the top ω_m of the band, we have $y \ll 1$ and

$$g(n) = (y/4)^{|n|}[1 + y/2 + 3y^2/8 + \cdots] \times [1 + y/2 + 5y^2/16 + \cdots]^{|n|}. \quad (16)$$

In such a case, convergence of the series in Eq. (12) is very rapid and we need only consider a small defect space. In this limit, putting $n=1$ gives $\eta_1 \sim \frac{1}{2}$, which, when inserted back into Eq. (13), gives

$$(\omega_m/\omega_1)^2 = y = 1/[\tfrac{3}{4} + \tfrac{27}{16}\lambda] \ll 1 \quad (17)$$

so that $\lambda \gg \frac{4}{27}$. If $\lambda \gg \frac{4}{27}$, then Eq. (17) yields the eigenfrequency of the odd mode as a function of λ. The asymptotic expression for η_n with $n \geq 2$ is

$$\eta_n = (y^{|n-1|}/4^n)[2 + \lambda/2] \quad (18)$$

with $y \ll 1$. Thus the spatial localization of the mode is established at least for $y \ll 1$. The fact that $\eta_0 = 1$, $\eta_1 = \frac{1}{2}$, yet the other $\eta_n \sim 0$ is an indication that the vibrational character of the central atom and its neighbors behaves as a quasimolecule which undergoes a large excursion in contrast to the rest of the host atoms.

For the three-dimensional simple-cubic anharmonic lattice with nearest-neighbor interactions, we find the results to be essentially the same as described here for this one-dimensional case.[5] Although the nonexistence of a bound state or localized mode in a continuum 3D space for a scalar field is well known in nonlinear field theory as the Derrick theorem,[8] this theorem does not apply for nontopological solitons in a discrete 3D space.

Except for the amplitude α, the entire calculation for the localized-mode frequency has so far been based on classical lattice dynamics. For the discussion of thermal excitations of the localized mode and their bearing on the thermodynamic properties of anharmonic solids, a quantum mechanical treatment is required. We assume that these points, which can be formulated by the introduction of, for example, the method of the double-time Green's function,[1] carry over from classical to quantum mechanics in the usual way.

The production of these localized modes requires the crystal energy to be increased over that found for the perfect crystal, but associated with the defect is crystal disorder which gives rise to an additional configurational entropy, S_c. For a localized defect, the Helmholtz free energy is given by

$$F = F_0 + nf - TS_c, \quad (19)$$

where F_0 describes the contribution from the perfect crystal, nf is the work done in the creation of n defects, and $-TS_c$ gives the contribution from the disorder. Minimization of the free energy with respect to the number of defects n for the limit where $n \ll N$ gives[9]

$$n \approx N \exp(-f/k_B T). \quad (20)$$

For the strongly-localized-mode limit, the number of these modes present at any temperature in a sample of constant volume is given by Eq. (20) with the free energy per defect

$$f_l = \Delta\epsilon - T\Delta s_v, \quad (21)$$

where $\Delta\epsilon$ is made up of two terms: one from the change in the mean vibrational energy of the spectrum and the other from the change in the volume. At $T=0$ K, the zero-point local-mode spectrum is unpopulated so that the vibrational ground state is described by a spectrum of plane-wave modes. In the low-temperature limit, the difference between the two vibrational configurations can be characterized completely in terms of the extra zero-point energy contribution required to form the anharmonic localized excitation spectrum. Since at low temperatures $\Delta s_v = s(\text{localized}) - s(\text{plane}) \approx 0$, then $f_l = \Delta\epsilon$ in Eq. (20).

It is expected that these localized modes can move from site to site so that the lattice can recover the translational symmetry once destroyed. We now consider two classes of physical systems where evidence for these modes exists: quantum crystals and defects in alkali halides.

Let us first examine solid ^{4}He and ^{3}He. For these systems the present formalism based on conventional, classical lattice dynamics does not apply[10]; however, if we reinterpret the potential energy of our simple lattice as representing an effective potential energy for the quantum system,[11] then some comparisons between experiment and our model are possible. After the effective harmonic potential is adjusted to agree with the experimental frequencies under consideration, our results, in a qualitative sense, may be used to describe intrinsic localized modes in solid ^{4}He and ^{3}He.

In 1962 an anomalous extra contribution to the crystal specific heat of bcc ^{3}He was found[12,13] that was assigned to vacancy production. These measurements have been confirmed and extended by others.[14,15] Recently, a direct determination of the thermal vacancy concentration of ^{3}He and ^{4}He has been obtained from measurements of the temperature dependence of the x-ray lattice parameter in a constant-volume cell.[16,17] One underlying problem has been that the energy for vacancy generation is measured to be much smaller than the Debye energy of the solid. Note that Eq. (20) has the same form as for the vacancy result. In addition, the energy required to generate an anharmonic localized mode depends essentially on the energy difference between the zero-point energies of the two different kinds of modes; thus a small activation free energy occurs automatically. This activated process should provide a contribution to the specific heat in addition to that associated with vacancy waves[18] in quantum crystals.

The addition of point defects to anharmonic crystals is expected to have a dramatic effect on the translational motion of the intrinsic local modes since these extrinsic defects would act as strain-field traps. The interplay of the thermal energy with this combination of traps and mode translation should give an unexpected complexity to defect dynamics. This binding may provide a simple explanation for the puzzling experimental result found for Ag^+ in KI where two elastic configurations[19] are observed to occur for this point defect at low temperatures. We speculate that the Ag^+ ion is on center in the KI host at 1.2 K only because a large-amplitude intrinsic breathing mode is trapped at the impurity site. When this anharmonic mode escapes from the defect at $\simeq 20$ K, the increase in the local volume available to the Ag^+ ion permits it to move to the observed off-center configuration.[19]

For many years workers have looked without apparent success for experimental evidence of dramatic anharmonic effects in quantum crystals. Although most anharmonic vibrational modes appear to be similar to renormalized harmonic modes,[10] our work shows that the anharmonicity is directly responsible for the occurrence of intrinsic localized modes at finite temperature. Because these localized modes have a larger zero-point amplitude than the plane-wave modes that they replace, the resulting activated process produces localized volume changes in the solid. Finally, the localized strain fields associated with point defects in crystals may attract or repel these intrinsic localized modes.

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