Surface phonons and other localized excitations

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The diatomic linear chain of masses coupled by harmonic springs is a textbook model for vibrational normal modes (phonons) in crystals. In addition to propagating acoustic and optic branches, this model is known to support a ''gap mode'' localized at the surface, provided the atom at the surface has light rather than heavy mass. An elementary argument is given which explains this mode and provides values for the frequency and localization length. By reinterpreting this mode in different ways, we obtain the frequency and localization length for three other interesting modes: (1) the surface vibrational mode of a light mass impurity at the surface of a monatomic chain; (2) the localized vibrational mode of a stacking fault in a diatomic chain; and (3) the localized vibrational mode of a light mass impurity in a monatomic chain. © *2000 American Association of Physics Teachers.*

I. INTRODUCTION

Unlike molecules which have discrete vibrational frequencies, crystals have a continuous spectrum of vibrations which can propagate as traveling waves.[1–3] This fact causes crystals to be much better heat conductors than glasses or liquids. Sometimes the spectrum is interrupted by gaps where no propagating normal modes occur. Other interesting behavior happens at frequencies inside the gap, such as localized (non-propagating) normal modes associated with defects and surfaces. The text by Ziman[4] has a good discussion. A visualization of surface modes on the (100) surface of Cu is on the website of Ch. Wöll, Ruhr-Universität Bochum.[5] The present paper shows how this happens for some particular cases of one-dimensional crystals, or linear chains of atoms. Our treatment uses only classical mechanics, and gives properties (frequency and displacement pattern) rigorously by pictorial arguments with no higher algebra.

The surface phonon provides the simplest example of wave localization, an effect which occurs in many branches of physics. Analogous phenomena are found in the quantum treatment of electrons in single-particle approximation,[1,2] and in the new field of ''photonic band-gap systems.''[6] This paper reports a simple way of understanding the surface phonon on the diatomic linear chain. The model is then extended and reinterpreted to give simple explanations of some other localized modes.

II. DIATOMIC MOLECULE

A diatomic molecule has a single vibrational ''normal mode.'' Even though the restoring force of atom 1 on atom 2 has in reality a complicated quantum-mechanical origin, for small displacements away from equilibrium it can always be well approximated by a spring obeying Hooke's law with a spring constant K. Using standard physics of the two-body problem,[7] if the two atoms have masses M_H and M_L (H and L are for heavy and light), the squared oscillation frequency ω^2 is K/M_{red}, where M_{red} is the ''reduced mass'' $M_L M_H/(M_L+M_H)$.

III. PERFECT INFINITE CHAINS

A crystalline solid is a very large molecule, with a continuous spectrum (or band) of vibrational frequencies. Solids can also be modeled by masses connected to each other by springs. A one-dimensional chain of masses is often studied, not because it is found in nature, but because the mathematics is simple and can be generalized to more realistic three-dimensional arrangements. For a large enough collection of atoms, most of the vibrational normal modes are classified as ''bulk'' normal modes, which means they are essentially identical to those of a hypothetical infinite sample with no boundaries. Each ''bulk'' normal mode has a pattern of atomic displacements which extends throughout the system. Similar to the normal modes of a vibrating string, these are sine and cosine standing waves. Alternately, one can use linear combinations of sines and cosines to give an equivalent basis of left- and right-going traveling waves. For the case of all masses equal to M_0, the lth atom (located at $R_l = la$) has a displacement $A \sin(kR_l - \omega_k t)$ in a right-going traveling wave. The corresponding squared frequency is $(4K/M_0)\sin^2(ka/2)$. There are as many such solutions (N) as there are atoms in the chain, namely solutions for each k in the range $(-\pi/a, \pi/a)$. This is derived in many texts.[1–3,8] For $N \to \infty$ the spectrum is continuous between the minimum squared frequency of zero and the maximum of $\omega_{\text{max}}^2 = 4K/M_0$. A particularly original discussion is given by Martinez.[9]

The vibrational spectrum of a real material sometimes has a gap, an interval of frequencies where there are no traveling wave solutions. A simple model illustrating this is the ''diatomic chain,'' an infinite chain of alternating masses M_L, M_H. The algebra, which is more complicated than the monatomic chain, is also given in texts.[1,3] The dispersion curve for ω_k^2 is given in Fig. 1. There are now two ''branches,'' labeled acoustic and optic, and a gap. Exactly in the middle of the gap, the surface may induce a *localized* vibrational normal mode, with amplitude which falls exponentially $[\propto \exp(-R/\xi)]$ with distance R into the bulk.

Before discussing this, we sharpen our understanding with a quantitative interpretation of the four special bulk modes
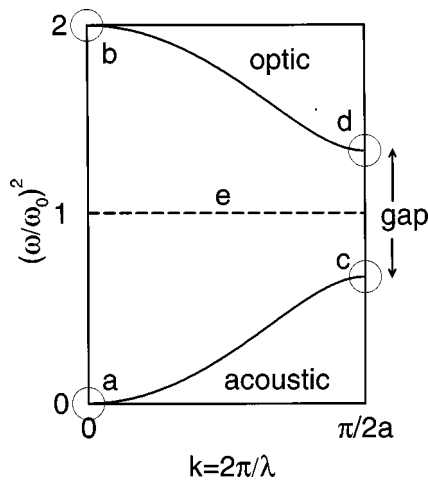
Fig. 1. Dispersion of squared frequency (in units $\omega_0^2 = K/M_{\mathrm{red}}$) vs wave vector k for the diatomic chain. The gap is proportional to $(M_H - M_L)/(M_H + M_L)$, and is drawn for the case $M_H = 2M_L$. The distance between atoms is a. The dashed line shows the position of the surface mode.

indicated by circles in Fig. 1. The frequencies of these special modes can be understood without the algebra needed to find the frequencies of the modes at general k vectors.

IV. SPECIAL BULK MODES

The four special modes circled in Fig. 1 have the simple vibrational patterns shown in Fig. 2. First, why are these patterns ''normal modes''? If we take, as initial conditions, the velocities of all atoms to be zero and the positions to be as shown in Fig. 2, then Newton's laws have simple, and perhaps even obvious solutions: The pattern is preserved, and oscillates in time as $\cos(\omega t)$ for some special choice of ω. This is the *definition* of a normal mode. Second, what is the corresponding frequency of oscillation? This can be answered by careful consideration of forces and masses.
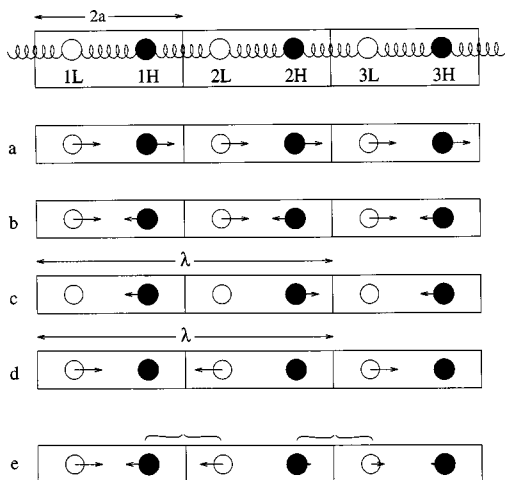

Fig. 2. The diatomic chain, the special bulk modes a, b with wavelength $\lambda = \infty$ and wave vector $k = 0$, the special bulk modes c, d with wavelength $\lambda = 4a$ and $k = \pi/2a$ (all shown circled in Fig. 1), and the gap mode e confined at the surface when a light atom terminates the chain. In pictures a–d, the chain is infinite; by contrast, in picture e, the light atom at the left is the surface atom, with no spring acting to its left. The brackets indicate pairs of atoms which move without altering the length of the bond between them.

Mode a: This is the simplest mode with all atoms having the same displacement. This has infinite wavelength (zero wave vector), no stretch of any spring, and therefore zero restoring force and $\omega = 0$.

Mode b: This has oppositely directed displacements for adjacent atoms. Each unit cell of the crystal has the same displacement pattern. Therefore the wavelength is infinite and the wave vector is zero. The displacements in mode b are such that u_L (the displacement of the light atom) is proportional to M_H, and similarly u_H is proportional to M_L. Thus the center of mass of each unit cell is fixed. The mode is almost the same as in a diatomic molecule, except each atom has two springs attached, one stretched and the other compressed by the same amount. Therefore, when released from rest, each pair of atoms oscillates with fixed center of mass but with twice the restoring force of an isolated diatomic molecule, i.e., $\omega^2 = 2K/M_{\mathrm{red}}$. This is the highest frequency normal mode in the spectrum.

Mode c: This has light atoms stationary and heavy atoms moving in an alternating pattern. The light atoms feel equal and opposite forces which cancel, while the heavy atoms feel repulsive and attractive forces which add. This pattern also oscillates in time, with squared frequency $\omega^2 = 2K/M_H$.

Mode d: This is the same as mode c except heavy and light atoms are interchanged, making the squared frequency equal to $2K/M_L$. Modes c and d have wavelength $4a$ and wave vector $\pi/2a$. All other normal modes of the infinite crystal are more complicated and have frequencies which lie on smooth curves connecting these four modes.

V. SURFACE MODE IN THE GAP

Modes which are confined to the surface region normally must have frequencies which lie outside the ''bulk'' bands. Discussions of such modes are given in texts on surface physics[10–14] and measurements are cataloged by Kress and de Wette.[15] We have discovered a very simple explanation of the fact[16] that a ''gap mode'' confined to the surface occurs in the diatomic chain if the endmost atom is a light atom.

Consider mode e, which like mode b has pairs of atoms vibrating with fixed center of mass. However, adjacent *pairs* vibrate in such a way that the connecting spring is not stretched. Thus each pair experiences no force from any other atom and is decoupled from the rest of the chain. The resulting decoupled pairs oscillate with $\omega^2 = K/M_{\mathrm{red}}$ as for isolated diatomic molecules. Since all pairs have the same frequency, this is a stable normal mode. The frequency lies exactly in the middle of the gap of the squared frequency spectrum $[K/M_{\mathrm{red}} = (1/2)(2K/M_L + 2K/M_H)]$. In order to be decoupled, the heavy atom of a given pair, and the adjacent light atom of the next pair deeper into the bulk, must have the same displacement, smaller by M_L/M_H (and with opposite sign) than the displacement of the previous light atom closer to the surface, in order to conserve center of mass position. Since adjacent pairs have displacement ratios $-M_L/M_H$, the nth pair has amplitude proportional to $(-M_L/M_H)^n = (-1)^n \exp(-n \ln(M_H/M_L))$. This is an exponential decay $\exp(-2na/\xi)$ with decay length $\xi = 2a/\ln(M_H/M_L)$. If the surface atom had been a heavy atom, this mode would have been exponentially growing rather than decaying, which is not allowed for a normal mode. Mode e was first found by Wallis[16] in an elegant calculation of the spectrum of finite chains. Our simple ar-
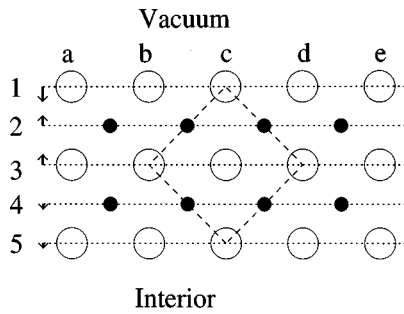
Fig. 3. ''Polar'' surface of a diatomic crystal in two dimensions. This is a two-dimensional analog of the ''(111)'' surface of crystals with the ''rock-salt'' (NaCl) structure. A square conventional unit cell is shown as dashed lines parallel to conventional $\hat{x}$ and $\hat{y}$ axes. There are two possible terminations of such crystals, ones which expose planes of light atoms as shown by open circles, and ones which expose planes of heavy atoms, shown as closed circles. Since the heavy and light atoms have opposite ionic charges, such surfaces have a surface dipole and are called polar.

gument is not (to our knowledge) in the literature. A ''standard'' derivation is given in the text by Cottam and Tilley.[12]

VI. SURFACE MODES OF THREE-DIMENSIONAL CRYSTALS

Mode e is directly related to a *branch* of surface normal modes of higher-dimensional diatomic crystals. A two-dimensional version is shown in Fig. 3. Various types of surfaces are possible for such crystals. If cut perpendicular to a conventional $\hat{x}$ or $\hat{y}$ axis shown in Fig. 3 by dashed lines, the surface contains equal numbers of A and B ions, and is referred to as ''nonpolar.'' By contrast, the surface shown is a ''polar surface'' with a layer of light atoms exposed and layers of heavy and light atoms alternating underneath. There is a vibrational normal mode in which each *layer* oscillates perpendicular to the surface (as indicated by arrows) and which is localized at the surface. Of course, in real crystals the forces extend beyond first neighbors, so the displacement ratio $(-M_L/M_H)$ may not be exactly obeyed and the squared frequency may not lie exactly at mid-gap, but the actual behavior will mimic reasonably well the idealized one-dimensional example of Sec. V.

There is actually not just one mode of this type, but a *branch* of such modes, with displacement patterns sinusoidally modulated along the surface. The one depicted in Fig. 3 has the surface atoms ''a,'' ''b,'' ''c,'' all moving in phase, corresponding to an infinite wavelength, or zero wave vector, parallel to the surface. The other extreme case of modulation is when atoms along the surface are completely out of phase; when atom ''a'' moves down, atom ''b'' moves up, and so forth, corresponding to a wavelength $\lambda = 2\sqrt{2}a$ in the plane of the surface. Thus we anticipate a branch of surface excitations with wave vectors lying in the plane of the surface. In order for such a mode to be exponentially localized in the surface region, the frequency of oscillation must lie in a gap where there are no corresponding bulk normal modes with the same components of wave vector in the plane of the surface. A gap is almost certain to occur for the case of zero wave vector, but at increasing wave vectors the gap may disappear, and the mode ceases to be localized near the surface.

Dimension two or three also opens new possibilities less directly related to one-dimensional models, such as surface
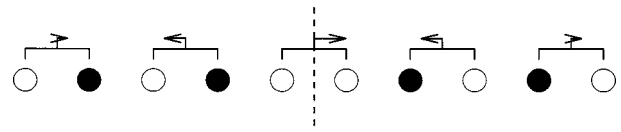

Fig. 4. Localized normal mode of vibration of the diatomic chain with a stacking fault, obtained from mode e of Fig. 2 by reflecting the lattice and assigning $u(-l) = u(l)$.

normal modes with displacements in the plane of the surface. Many branches of surface normal modes have been seen experimentally by scattering experiments. Unfortunately we have not been able to locate in the literature any observation of the simple mode illustrated in Fig. 3. This is perhaps because polar surfaces are relatively unstable and hard to create and work with.

VII. IMPURITY ATOM ON THE SURFACE

Another known result is that a surface mode appears above the bulk frequency spectrum for a monatomic chain, provided the atom on the surface is lighter than the rest by at least a factor of 2. This can be proven by a reinterpretation of the previous construction. For mode e in Fig. 2, let the two atoms connected by the unstretched spring be reinterpreted as a single atom of mass $M_0 = M_H + M_L$. Then the model has new interior atoms all with mass M_0, but a surface impurity atom with mass $M_{imp} = M_L < 0.5 M_0$. The surface mode e still solves Newton's laws with $\omega_S^2 = K/M_{red}$ and $M_{red} = M_L M_H/(M_L + M_H)$. In terms of the new variables M_{imp} and M_0 the reduced mass M_{red} is $M = M_{imp}(M_0 - M_{imp})/M_0$. The frequency ω_S^2 lies above the top of the bulk band ($\omega_{max}^2 = 4K/M_0$) if $M_0 > 2M_{imp}$, and merges into the bulk band for $M_0 \leq 2M_{imp}$. This result seems also to have been first discovered by Wallis.[17] A ''standard'' proof of this result is in the book by Desjonquères and Spanjaard.[11]

VIII. LOCALIZED GAP MODE OF A STACKING FAULT

The gap mode e of Fig. 2 generates a corresponding mode of a defective bulk crystal, shown in Fig. 4. This mode decays exponentially in both directions away from the center of symmetry. This center lies in the middle of a ''stacking fault'' where two light-mass atoms have been put adjacent to each other. It is a one-dimensional version of a planar defect which occurs in real three-dimensional crystals. The quantum-mechanical force between two light-mass atoms differs from the force which binds the atoms of unlike mass. Therefore, we must expect that the separation a' of the light-mass atoms will differ from the equilibrium separation a of unlike atoms, and that the force constant K' between these atoms will differ from the constant K occurring elsewhere. Notice that for the special displacement pattern of Fig. 4, there is no force between the adjacent light atoms, so the values of a' and K' are irrelevant; the squared frequency of the normal mode is exactly the same as the surface mode e of Fig. 2, and is pinned at midgap.

The stacking fault is a simple example of a ''topological defect,'' that is, a defect which cannot be transformed away by any local change. As far as we know, the midgap normal mode of vibration found here for the stacking fault has not

previously been discussed in the literature. However, a close analog is the ''topological soliton'' found at midgap in the electronic spectrum of the ''Su–Schrieffer–Heeger'' model[18] for polyacetylene with a topological defect in the pattern of dimerization of carbon–carbon bonds along the chain.

IX. LOCALIZED VIBRATION OF A LIGHT MASS IMPURITY IN A MONATOMIC CHAIN

Suppose an impurity of mass $M_{\mathrm{imp}} < M_0$ is substituted into a monatomic chain of mass M_0 with no change in force constants. Define the fractional mass deficit to be $\epsilon = (M_0 - M_{\mathrm{imp}})/M_0 > 0$. It is known that this system supports a localized mode whose frequency ''splits off'' above the frequency $\omega_{\max}$ of the uppermost bulk mode. Specifically, the mode has squared frequency $\omega_{\max}^2/(1-\epsilon^2)$ and is localized around the impurity with localization length $a/\ln((1+\epsilon)/(1-\epsilon))$. The earliest presentation of this mode known to us is by Montroll and Potts.[19] The topic of localized modes in solids had been given a systematic formulation in three earlier papers by Lifshits, available only in Russian.[20] A textbook derivation is given by Mihály and Martin,[21] and a nice qualitative discussion is given by Harrison.[22]

These results follow rigorously by reinterpretation of Fig. 4. Simply regard each pair of co-moving atoms as a single atom whose mass is the sum of the two shown in the figure. Thus M_0 is $M_H + M_L$, M_{imp} is $2M_L$, and the new lattice constant a is twice the previous distance a. When the impurity mass is heavier than the host mass, there is no longer a split-off bound state, but instead a ''resonance'' within the bulk band.

In three-dimensional crystals the occurrence of a vibrational bound state requires a minimum mass deficit ϵ which is model dependent, whereas our one-dimensional (1D) example has a bound state for arbitrarily small mass deficit. This is a classical discrete-system analog of the continuum quantum-mechanical theorem that an attractive well always has a bound state in a 1D one-electron problem (and also in two dimensions) but requires a critical well-depth in three dimensions.[23] For the impurity on the surface, however, we saw that even in one dimension there is a critical mass deficit of 1/2. The quantum analog is that if the well is at the edge of a 1D half space (the other half of the space is impenetrable because of an infinite potential), then there is a critical well depth, equal to the well depth at which the second bound state appears for the symmetric well in the full 1D space.

X. SUMMARY

Two simple surface phonons and two simple bound defect modes in one-dimensional lattices have been quantitatively explained by pictorial construction and elementary physics of the two-body problem. This is certainly not a complete catalog of interesting localized modes, but we think that these modes can serve as useful pedagogical models for phenomena in several branches in physics.

[1]C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1996), 7th ed., see especially pp. 99–100.

[2]N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).

[3]H. Ibach and H. Lüth, *Solid State Physics* (Springer-Verlag, Berlin, 1991).

[4]J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U.P., Cambridge, 1972), 2nd ed., pp. 71–76.

[5]url: http://marvin1.pc.ruhr-uni-bochum.de/ deutsch/LM_10.htm Click on the dispersion curve of the desired mode at a desired wave vector to display the corresponding atomic motions.

[6]J. D. Joannopoulos, R. D. Meade, and J. N. Winn, *Photonic Crystals: Molding the Flow of Light* (Princeton U.P., Princeton, 1995).

[7]For example, A. P. French, *Newtonian Mechanics* (Norton, New York, 1965), p. 405ff.

[8]H. Goldstein, *Classical Mechanics* (Addison–Wesley, Reading, MA, 1980).

[9]E. N. Martinez, ''Effective Mass of a Classical Linear Chain,'' Am. J. Phys. **61**, 1102–1110 (1993).

[10]A. Zangwill, *Physics at Surfaces* (Cambridge U.P., Cambridge, 1988).

[11]M.-C. Desjonquères and D. Spanjaard, *Concepts in Surface Physics* (Springer-Verlag, Berlin, 1993), Chap. 4.

[12]M. G. Cottam and D. R. Tilley, *Introduction to Surface and Superlattice Excitations* (Cambridge U.P., Cambridge, 1989), pp. 36–40.

[13]H. Lüth, *Surfaces and Interfaces of Solid Materials* (Springer-Verlag, Berlin, 1995).

[14]S. G. Davison and M. Stęślicka, *Basic Theory of Surface States* (Oxford U.P., Oxford, 1992).

[15]W. Kress and F. W. de Wette, eds., *Surface Phonons* (Springer-Verlag, Berlin, 1991).

[16]R. F. Wallis, ''Effect of Free Ends on the Vibration Frequencies of One-Dimensional Lattices,'' Phys. Rev. **105**, 540–545 (1957).

[17]R. F. Wallis, ''Lattice Dynamics of Crystal Surfaces,'' in *Progress in Surface Science*, edited by S. G. Davison (Pergamon, Oxford, 1973), Vol. 4, part 3.

[18]A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, ''Solitons in conducting polymers,'' Rev. Mod. Phys. **60**, 781–850 (1988).

[19]E. W. Montroll and R. B. Potts, ''Effect of Defects on Lattice Vibrations,'' Phys. Rev. **100**, 525–543 (1955).

[20]I. M. Lifshits, J. Phys. (Moscow) **7**, 215 (1943); **7**, 249 (1943); **8**, 89 (1944).

[21]L. Mihály and M. C. Martin, *Solid State Physics: Problems and Solutions* (Wiley, New York, 1996), p. 21.

[22]W. A. Harrison, *Solid State Theory* (McGraw–Hill, New York, 1970; reprinted by Dover), p. 381ff.

[23]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Pergamon, Oxford, 1958), 2nd ed., p. 158.