# Vibrations (phonons) in a chain of identical atoms

# Simple model to see how phonons appear in solids, *acoustic* and *optical*.



## 1 Problem

In your quantum mechanics course you saw how the energies of a particle in a periodic potential has a peculiar structure of continuous bands separated by gaps of forbidden energies. This forms the basics for properties of metals and other materials. However, in real materials the atoms forming the lattice potential are not totally fixed. The atoms can move (oscillate) around their equilibrium positions, but since they interact with one another the vibrational motion of the atoms will be *collective* (the oscillate in wave-like ways). The simplest model for a solid is a chain formed from identical atoms, coupled to their neighbours with a spring, as shown in the figure below.

By assuming periodic boundary conditions this problem can be solved ex-

Assignment 4



Figure 1: In the upper chain the (identical) atoms are at equilibrium with an equal distance between every two neighbouring atoms (lattice spacing a). In the lower chain the n'th atom is displaced by an amount  $u_n$  from its equilibrium position  $R_n$ .

actly [1], and one finds the energies<sup>1</sup> (frequencies) of the collective oscillations. These are called *acoustic phonons* (see figure above). In this assignment I want that you write down the corresponding Hamiltonian (Lagrangian is also ok), and solve the equations-of-motion such that you get the energies. You are very welcome to also solve the same problem with two types of atoms, *i.e.* different masses. In this case you end up with a second branch of energies, the *optical phonons*. As literature I suggest the book [1] (I attach the relevant pages below), but the derivations can be found in many other books as well.

### References

 J. J. Quinn and K.-S. Yi, Solid State Physics, pages 37-44 and 48-50, (Springer, 2009).

<sup>&</sup>lt;sup>1</sup>Also called *dispersions*, denoted as  $\omega(k)$  where k is the wave-number of the vibrational wave.



So far, in our discussion of the crystalline nature of solids we have assumed 4 that the atoms sat at lattice sites. This is not actually the case; even at the 5 lowest temperatures the atoms perform small vibrations about their equilib-6 rium positions. In this chapter we shall investigate the vibrations of the atoms 7 in solids. Many of the significant features of lattice vibrations can be under-8 stood on the basis of a simple one-dimensional model, a monatomic linear 9 chain. For that reason we shall first study the linear chain in some detail. 10

We consider a linear chain composed of N identical atoms of mass M 11 (see Fig. 2.1). Let the positions of the atoms be denoted by the parameters 12  $R_i$ , i = 1, 2, ..., N. Here, we assume an infinite crystal of vanishing surface 13 to volume ratio, and apply *periodic boundary conditions*. That is, the chain 14 contains N atoms and the Nth atom is connected to the first atom so that 15

$$R_{i+N} = R_i. (2.1) 16$$

The atoms interact with one another (e.g., through electrostatic forces, core 17 repulsion, etc.). The potential energy of the array of atoms will obviously be 18 a function of the parameters  $R_i$ , i.e., 19

$$U = U(R_1, R_2, \dots, R_N).$$
 (2.2)

We shall assume that U has a minimum  $U(R_1^0, R_2^0, \ldots, R_N^0)$  for some partic- 20 ular set of values  $(R_1^0, R_2^0, \ldots, R_N^0)$ , corresponding to the equilibrium state of 21 the linear chain. Define  $u_i = R_i - R_i^0$  to be the deviation of the *i*th atom from 22 its equilibrium position. Now expand U about its equilibrium value to obtain 23

$$U(R_1, R_2, \dots, R_N) = U\left(R_1^0, R_2^0, \dots, R_N^0\right) + \sum_i \left(\frac{\partial U}{\partial R_i}\right)_0 u_i$$
$$+ \frac{1}{2!} \sum_{i,j} \left(\frac{\partial^2 U}{\partial R_i \partial R_j}\right)_0 u_i u_j + \frac{1}{3!} \sum_{i,j,k} \left(\frac{\partial^3 U}{\partial R_i \partial R_j \partial R_k}\right)_0 u_i u_j u_k + \cdots$$
(2.3)

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Fig. 2.1. Linear chain of N identical atoms of mass M

The first term is a constant which can simply be absorbed in setting the 24 zero of energy. By the definition of equilibrium, the second term must vanish 25 (the subscript zero on the derivative means that the derivative is evaluated at 26  $u_1, u_2, \ldots, u_n = 0$ ). Therefore, we can write 27

$$U(R_1, R_2, \dots, R_N) = \frac{1}{2!} \sum_{i,j} c_{ij} u_i u_j + \frac{1}{3!} \sum_{i,j,k} d_{ijk} u_i u_j u_k + \dots, \qquad (2.4)$$

where

$$c_{ij} = \left(\frac{\partial^2 U}{\partial R_i \partial R_j}\right)_0,$$
  
$$d_{ijk} = \left(\frac{\partial^3 U}{\partial R_i \partial R_j \partial R_k}\right)_0.$$
 (2.5)

For the present, we will consider only the first term in (2.4); this is called *the* 29 harmonic approximation. The Hamiltonian in the harmonic approximation is 30 31

$$H = \sum_{i} \frac{P_i^2}{2M} + \frac{1}{2} \sum_{i,j} c_{ij} u_i u_j.$$
 (2.6) 32

Here,  $P_i$  is the momentum and  $u_i$  the displacement from the equilibrium position of the *i*th atom. 34

#### Equation of Motion

Hamilton's equations

$$\dot{P}_{i} = -\frac{\partial H}{\partial u_{i}} = -\sum_{j} c_{ij} u_{j},$$
$$\dot{u}_{i} = \frac{\partial H}{\partial P_{i}} = \frac{P_{i}}{M}.$$
(2.7)

can be combined to yield the equation of motion

$$M\ddot{u}_i = -\sum_j c_{ij} u_j. \tag{2.8}$$

In writing down the equation for  $\dot{P}_i$ , we made use of the fact that  $c_{ij}$  actually 38 depends only on the relative positions of atoms *i* and *j*, i.e., on |i - j|. Notice 39 that  $-c_{ij}u_j$  is simply the force on the *i*th atom due to the displacement 40  $u_j$  of the *j*th atom from its equilibrium position. Now let  $R_n^0 = na$ , so that 41  $R_n^0 - R_m^0 = (n-m)a$ . We assume a solution of the coupled differential equations 42

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2.1 Monatomic Linear Chain 39

of motion, (2.8), of the form

$$u_n(t) = \xi_q e^{i(qna - \omega_q t)}.$$
(2.9)

By substituting (2.9) into (2.8) we find

$$M\omega_q^2 = \sum_m c_{nm} \mathrm{e}^{\mathrm{i}q(m-n)a}.$$
 (2.10)

Because  $c_{nm}$  depends only on l = m - n, we can rewrite (2.10) as

$$M\omega_q^2 = \sum_{l=1}^N c(l) e^{iqla}.$$
 (2.11) 46

**Boundary** Conditions

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We apply periodic boundary conditions to our chain; this means that the 48 chain contains N atoms and that the Nth atom is connected to the first atom 49 (Fig. 2.2). This means that the (n + N)th atom is the same atoms as the nth 50 atom, so that  $u_n = u_{n+N}$ . Since  $u_n \propto e^{iqna}$ , the condition means that 51

$$e^{iqNa} = 1, (2.12)$$

or that  $q = \frac{2\pi}{Na} \times p$  where  $p = 0, \pm 1, \pm 2, \ldots$ . However, not all of these values 52 of q are independent. In fact, there are only N independent values of q since 53 there are only N degrees of freedom. If two different values of q, say q and q' 54 give identical displacements for every atom, they are equivalent. It is easy to 55 see that 56





Fig. 2.2. Periodic boundary conditions on a linear chain of N identical atoms

for all values of n if  $q' - q = \frac{2\pi}{a}l$ , where  $l = 0, \pm 1, \pm 2, \ldots$  The set of inde- 57 pendent values of q are usually taken to be the N values satisfying  $q = \frac{2\pi}{L}p$ , 58 where  $-\frac{N}{2} \leq p \leq \frac{N}{2}$ . We will see later that in three dimensions the inde- 59 pendent values of  $\mathbf{q}$  are values whose components  $(q_1, q_2, q_3)$  satisfy  $q_i = \frac{2\pi}{L_i}p$ , 60 and which lie in the first Brillouin zone, the Wigner–Seitz unit cell of the 61 reciprocal lattice. 62

#### Long Wave Length Limit

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Let us look at the long wave length limit, where the wave number q tends to 64 zero. Then  $u_n(t) = \xi_0 e^{-i\omega_{q=0}t}$  for all values of n. Thus, the entire crystal is 65 uniformly displaced (or the entire crystal is translated). This takes no energy 66 if it is done very very slowly, so it requires  $M\omega^2(0) = \sum_{l=1}^{N} c(l) = 0$ , or 67  $\omega(q=0) = 0$ . In addition, it is not difficult to see that since c(l) depends only 68 on the magnitude of l that 69

$$M\omega^{2}(-q) = \sum_{l} c(l) e^{-iqla} = \sum_{l'} c(l') e^{iql'a} = M\omega^{2}(q).$$
(2.14)

In the last step in this equation, we replaced the dummy variable l by l' and 70 used the fact that c(-l') = c(l'). Equation (2.14) tells us that  $\omega^2(q)$  is an even 71 function of q which vanishes at q = 0. If we make a power series expansion 72 for small q, then  $\omega^2(q)$  must be of the form 73

$$\omega^2(q) = s^2 q^2 + \cdots \tag{2.15}$$

The constant s is called the *velocity of sound*.

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#### Nearest Neighbor Forces: An Example

So far, we have not specified the interaction law among the atoms; (2.15) 76 is valid in general. To obtain  $\omega(q)$  for all values of q, we must know the 77 interaction between atoms. A simple but useful example is that of nearest 78 neighbor forces. In that case, the equation of motion is 79

$$M\omega^{2}(q) = \sum_{l=1}^{1} c_{l} \mathrm{e}^{\mathrm{i}qla} = c_{-1} \mathrm{e}^{-\mathrm{i}qa} + c_{0} + c_{1} \mathrm{e}^{\mathrm{i}qa}.$$
 (2.16)

Knowing that  $\omega(0) = 0$  and that  $c_{-l} = c_l$  gives the relation  $c_1 = c_{-1} = -\frac{1}{2}c_0$ . 80 Therefore, (2.16) is simplified to 81

$$M\omega^{2}(q) = c_{0} \left[ 1 - \left( \frac{e^{iqa} + e^{-iqa}}{2} \right) \right].$$
 (2.17)

Since  $1 - \cos x = 2\sin^2 \frac{x}{2}$ , (2.17) can be expressed as

$$\omega^2(q) = \frac{2c_0}{M} \sin^2 \frac{qa}{2},$$
(2.18)

which is displayed in Fig. 2.3. By looking at the long wave length limit, the 83 coupling constant is determined by  $c_0 = \frac{2Ms^2}{a^2}$ , where s is the velocity of 84 sound.

BookID 160928\_ChapID 02\_Proof# 1 - 29/07/09

2.2 Normal Modes 41



Fig. 2.3. Dispersion relation of the lattice vibration in a monatomic linear chain

#### 2.2 Normal Modes

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The general solution for the motion of the nth atom will be a linear com- 87 bination of solutions of the form of (2.9). We can write the general solution 88 as 89

$$u_n(t) = \sum_q \left[ \xi_q \mathrm{e}^{\mathrm{i}qna - \mathrm{i}\omega t} + \mathrm{cc} \right], \qquad (2.19)$$

where cc means the complex conjugate of the previous term. The form of (2.19) 90 assures the reality of  $u_n(t)$ , and the 2N parameters (real and imaginary parts 91 of  $\xi_q$ ) are determined from the initial values of the position and velocity of 92 the N atoms which specify the initial state of the system. 93

In most problems involving small vibrations in classical mechanics, we seek 94 new coordinates  $p_k$  and  $q_k$  in terms of which the Hamiltonian can be written 95 96 as

$$H = \sum_{k} H_{k} = \sum_{k} \left[ \frac{1}{2M} p_{k} p_{k}^{*} + \frac{1}{2} M \omega_{k}^{2} q_{k} q_{k}^{*} \right].$$
(2.20)

In terms of these normal coordinates  $p_k$  and  $q_k$ , the Hamiltonian is a sum 97 of N independent simple harmonic oscillator Hamiltonians. Because we use 98 running waves of the form  $e^{iqna-i\omega_q t}$  the new coordinates  $q_k$  and  $p_k$  can be 99 complex, but the Hamiltonian must be real. This dictates the form of (2.20). 100 101

The normal coordinates turn out to be

$$q_k = N^{-1/2} \sum_n u_n \mathrm{e}^{-\mathrm{i}kna},$$
 (2.21) 102

and

$$p_k = N^{-1/2} \sum_n P_n e^{+ikna}.$$
 (2.22) 104

We will demonstrate this for  $q_k$  and leave it for the student to do the same 105 for  $p_k$ . We can write (2.19) as 106

$$u_n(t) = \alpha \sum_k \xi_k(t) e^{ikna}, \qquad (2.23)$$

where  $\xi_k$  is complex and satisfies  $\xi_{-k}^* = \xi_k$ . With this condition  $u_n(t)$ , given 107 by (2.23), is real and  $\alpha$  is simply a constant to be determined. We can write 108 the potential energy  $U = \frac{1}{2} \sum_{mn} c_{mn} u_m u_n$  in terms of the new coordinates 109  $\xi_k$  as follows. 110

$$U = \frac{1}{2} |\alpha|^2 \sum_{mn} c_{mn} \sum_{k} \xi_k e^{ikma} \sum_{k'} \xi_{k'} e^{ik'na}.$$
 (2.24)

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Now, let us use k' = q - k to rewrite (2.24) as

$$U = \frac{1}{2} |\alpha|^2 \sum_{nkq} \left[ \sum_m c_{mn} \mathrm{e}^{\mathrm{i}k(m-n)a} \right] \xi_k \xi_{q-k} \mathrm{e}^{\mathrm{i}qna}.$$
(2.25)

From (2.10) one can see that the quantity in the square bracket in (2.25) is 112 equal to  $M\omega_k^2$ . Thus, U becomes 113

$$U = \frac{1}{2} |\alpha|^2 \sum_{nkq} M \omega_k^2 \xi_k \xi_{k-q}^* e^{iqna}.$$
 (2.26)

The only factor in (2.26) that depends on n is  $e^{iqna}$ . It is not difficult to prove 114 that  $\sum_{n} e^{iqna} = N\delta_{q,0}$ . We do this as follows: Define  $S_N = 1 + x + x^2 + \dots + 115$  $x^{N-1}$ ; then  $xS_N = x + x^2 + \dots + x^N$  is equal to  $S_N - 1 + x^N$ . 116

$$xS_N = S_N - 1 + x^N. (2.27)$$

$$S_N = \frac{1 - x^N}{1 - x}.$$
 (2.28)

Solving for  $S_N$  gives Now, let  $x = e^{iqa}$ . Then, (2.28) says N-1

$$\sum_{n=0}^{N-1} \left( e^{iqa} \right)^n = \frac{1 - e^{iqaN}}{1 - e^{iqa}}.$$
 (2.29)

Remember that the allowed values of q were given by  $q = \frac{2\pi}{Na} \times \text{integer}$ . 119 Therefore,  $iqaN = i\frac{2\pi}{Na}aN \times \text{integer}$ , and  $e^{iqaN} = e^{2\pi i \times \text{integer}} = 1$ . Therefore, 120 the numerator vanishes. The denominator does not vanish unless q = 0. When 121 q = 0,  $e^{iqa} = 1$  and the sum gives N. This proves that  $\sum_{n} e^{iqna} = N\delta(q, 0)$  122 when  $q = \frac{2\pi}{Na} \times$  integer. Using this result in (2.26) gives 123

2.2 Normal Modes 43

$$U = \frac{1}{2} |\alpha|^2 \sum_k M \omega_k^2 \xi_k \xi_k^* N.$$
 (2.30)

Choosing  $\alpha = N^{-1/2}$  puts U into the form of the potential energy for N 124 simple harmonic oscillators labeled by the k value. By assuming that  $P_n$  is 125 proportional to  $\sum_k p_k e^{-ikna}$  with  $p_{-k}^* = p_k$ , it is not difficult to show that 126 (2.22) gives the kinetic energy in the desired form  $\sum_k \frac{p_k p_k^*}{2M}$ . The inverse of 127 (2.21) and (2.22) are easily determined to be 128

$$u_n = N^{-1/2} \sum_k q_k \mathrm{e}^{\mathrm{i}kna}, \qquad (2.31) \quad _{129}$$

and

$$P_n = N^{-1/2} \sum_k p_k \mathrm{e}^{-\mathrm{i}kna}.$$
 (2.32) 131

#### Quantization

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Up to this point our treatment has been completely classical. We quantize the 133 system in the standard way. The dynamical variables  $q_k$  and  $p_k$  are replaced 134 by quantum mechanical operators  $\hat{q}_k$  and  $\hat{p}_k$  which satisfy the commutation 135 relation 136

$$[p_k, q_{k'}] = -i\hbar \delta_{k,k'}.$$
 (2.33)

The quantum mechanical Hamiltonian is given by  $H = \sum_{k} H_k$ , where 137

$$H_{k} = \frac{\hat{p}_{k}\hat{p}_{k}^{\dagger}}{2M} + \frac{1}{2}M\omega_{k}^{2}\hat{q}_{k}\hat{q}_{k}^{\dagger}.$$
 (2.34)

 $\hat{p}_k^{\dagger}$  and  $\hat{q}_k^{\dagger}$  are the Hermitian conjugates of  $\hat{p}_k$  and  $\hat{q}_k$ , respectively. They are 138 necessary in (2.34) to assure that the Hamiltonian is a Hermitian operator. 139 The Hamiltonian of the one-dimensional chain is simply the sum of N independent simple Harmonic oscillator Hamiltonians. As with the simple Harmonic 141 oscillator, it is convenient to introduce the operators  $a_k$  and its Hermitian 142 conjugate  $a_k^{\dagger}$ , which are defined by 143

$$u_k = \left(\frac{\hbar}{2M\omega_k}\right)^{1/2} \left(a_k + a_{-k}^{\dagger}\right), \qquad (2.35) \quad 144$$

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$$p_k = \imath \left(\frac{\hbar M \omega_k}{2}\right)^{1/2} \left(a_k^{\dagger} - a_{-k}\right).$$
(2.36) 146

The commutation relations satisfied by the  $a_k$ 's and  $a_k^{\dagger}$ 's are 147

$$\left[a_{k}, a_{k'}^{\dagger}\right]_{-} = \delta_{k,k'} \text{ and } \left[a_{k}, a_{k'}\right]_{-} = \left[a_{k}^{\dagger}, a_{k'}^{\dagger}\right]_{-} = 0.$$
 (2.37)

The displacement of the nth atom and its momentum can be written 148

$$u_n = \sum_k \left(\frac{\hbar}{2MN\omega_k}\right)^{1/2} e^{ikna} \left(a_k + a_{-k}^{\dagger}\right), \qquad (2.38) \quad 149$$

$$P_n = \sum_k \imath \left(\frac{\hbar\omega_k M}{2N}\right)^{1/2} e^{-ikna} \left(a_k^{\dagger} - a_{-k}\right).$$
 (2.39) 151

The Hamiltonian of the linear chain of atoms can be written

$$H = \sum_{k} \hbar \omega_k \left( a_k^{\dagger} a_k + \frac{1}{2} \right), \qquad (2.40)$$
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and its eigenfunctions and eigenvalues are

$$|n_1, n_2, \dots, n_N\rangle = \frac{\left(a_{k_1}^{\dagger}\right)^{n_1}}{\sqrt{n_1!}} \cdots \frac{\left(a_{k_N}^{\dagger}\right)^{n_N}}{\sqrt{n_N!}}|0\rangle,$$
 (2.41) <sup>155</sup>

and

$$E_{n_1,n_2,...,n_N} = \sum_i \hbar \omega_{k_i} \left( n_i + \frac{1}{2} \right).$$
 (2.42) 157

In (2.41),  $|0\rangle = |0_1\rangle |0_2\rangle \cdots |0_N\rangle$  is the ground state of the entire 158 system; it is a product of ground state wave functions for each harmonic 159 oscillator. It is convenient to think of the energy  $\hbar \omega_k$  as being carried by an 160 elementary excitations or quasiparticle. In lattice dynamics, these elementary 161 excitations are called phonons. In the ground state, no phonons are present 162 in any of the harmonic oscillators. In an arbitrary state, such as (2.41),  $n_1$  163 phonons are in oscillator  $k_1, n_2$  in  $k_2, \ldots, n_N$  in  $k_N$ . We can rewrite (2.41) as 164  $|n_1, n_2, \ldots, n_N\rangle = |n_1\rangle |n_2\rangle \cdots |n_N\rangle$ , a product of kets for each oscillator. 165

#### 2.3 Mössbauer Effect

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With the simple one-dimensional harmonic approximation, we have the tools 167 necessary to understand the physics of some interesting effects. One example 168 is the Mössbauer effect.<sup>1</sup> This effect involves the decay of a nuclear excited 169 state via  $\gamma$ -ray emission. First, let us discuss the decay of a nucleus in a free 170 atom; to be explicit, let us consider the decay of the excited state of Fe<sup>57</sup> via 171 emission of a 14.4 keV  $\gamma$ -ray.

$$\operatorname{Fe}^{57^*} \longrightarrow \operatorname{Fe}^{57} + \gamma.$$
 (2.43)

The excited state of Fe<sup>57</sup> has a lifetime of roughly  $10^{-7}$  s. The uncertainty 173 principle tells us that by virtue of the finite lifetime  $\Delta t = \tau = 10^{-7}$  s, there 174

<sup>&</sup>lt;sup>1</sup> R. L. Mössbauer, D.H. Sharp, Rev. Mod. Phys. **36**, 410–417 (1964).

We shall neglect terms of order  $N^{-2}$ ,  $N^{-3}$ ,..., etc. in this expansion. With 248 this approximation we can write 249

$$\langle n_i | \mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{R}_N} | n_i \rangle \simeq \prod_k \left[ 1 - \frac{E(K)}{\hbar\omega_k} \frac{n_k + \frac{1}{2}}{N} \right].$$
 (2.55)

To terms of order  $N^{-1}$ , the product appearing on the right-hand side of (2.55) 250 is equivalent to  $e^{-\frac{E(K)}{N}\sum_{k}\frac{n_{k}+\frac{1}{2}}{\hbar\omega_{k}}}$  to the same order. Thus, for the recoil free 251 fraction, we find 252

$$P(n_i, n_i) = e^{-2\frac{E(K)}{N}\sum_k \frac{n_k + \frac{1}{2}}{\hbar\omega_k}}.$$
 (2.56)

Although we have derived (2.56) for a simple one-dimensional model, the 254 result is valid for a real crystal if sum over k is replaced by a three-dimensional 255 sum over all **k** and over the three polarizations. We will return to the evaluation of the sum later, after we have considered models for the phonon spectrum 257 in real crystals. 258

#### 2.4 Optical Modes

So far, we have restricted our consideration to a monatomic linear chain. Later 260 on, we shall consider three-dimensional solids (the added complication is not 261 serious). For the present, let us stick with the one-dimensional chain, but let 262 us generalize to the case of two atoms per unit cell (Fig. 2.5). 263

If atoms A and B are identical, the primitive translation vector of the 264 lattice is a, and the smallest reciprocal vector is  $K = \frac{2\pi}{a}$ . If A and B are 265 distinguishable (e.g. of slightly different mass) then the smallest translation 266 vector is 2a and the smallest reciprocal lattice vector is  $K = \frac{2\pi}{2a} = \frac{\pi}{a}$ . In this 267 case, the part of the  $\omega$  vs. q curve lying outside the region  $|q| \leq \frac{\pi}{2a}$  must 268 be translated (or folded back) into the first Brillouin zone (region between 269  $-\frac{\pi}{2a}$  and  $\frac{\pi}{2a}$ ) by adding or subtracting the reciprocal lattice vector  $\frac{\pi}{a}$ . This 270 results in the spectrum shown in Fig. 2.6. Thus, for a non-Bravais lattice, the 271 phonon spectrum has more than one branch. If there are p atoms per primi-272 tive unit cell, there will be p branches of the spectrum in a one-dimensional 273 crystal. One branch, which satisfies the condition that  $\omega(q) \to 0$  as  $q \to 0$  is 274 called the *acoustic branch* or *acoustic mode*. The other (p-1) branches are 275 called *optical branches* or *optical modes*. Due to the difference between the



Fig. 2.5. Linear chain with two atoms per unit cell

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2.4 Optical Modes 49



Fig. 2.6. Dispersion curves for the lattice vibration in a linear chain with two atoms per unit cell



Fig. 2.7. Unit cells of a linear chain with two atoms per cell

pair of atoms in the unit cell when  $A \neq B$ , the degeneracy of the acoustic 276 and optical modes at  $q = \pm \frac{q}{2a}$  is usually removed. Let us consider a simple 277 example, the linear chain with nearest neighbor interactions but with atoms 278 of mass  $M_1$  and  $M_2$  in each unit cell. Let  $u_n$  be the displacement from its 279 equilibrium position of the atom of mass  $M_1$  in the *n*th unit cell; let  $v_n$  be 280 the corresponding quantity for the atom of mass  $M_2$ . Then, the equations of 281 motion are 282

$$M_1 \ddot{u}_n = K \left[ (v_n - u_n) - (u_n - v_{n-1}) \right], \qquad (2.57)$$

$$M_2 \ddot{v}_n = K \left[ (u_{n+1} - v_n) - (v_n - u_n) \right].$$
(2.58)

In Fig. 2.7, we show unit cells n and n + 1. We assume solutions of (2.57) and 283 (2.58) of the form 284

$$u_n = u_q \mathrm{e}^{\mathrm{i}q2an - \mathrm{i}\omega_q t},\tag{2.59}$$

$$v_n = v_a \mathrm{e}^{\mathrm{i}q(2an+a) - \mathrm{i}\omega_q t}.$$
(2.60)

where  $u_q$  and  $v_q$  are constants. Substituting (2.59) and (2.60) into the equations of motion gives the following matrix equation. 286



Fig. 2.8. Dispersion relations for the acoustical and optical modes of a diatomic linear chain

$$\begin{bmatrix} -M_1\omega^2 + 2K & -2K\cos qa\\ -2K\cos qa & -M_2\omega^2 + 2K \end{bmatrix} \begin{bmatrix} u_q\\ v_q \end{bmatrix} = 0.$$
 (2.61)

The nontrivial solutions are obtained by setting the determinant of the  $2 \times 2$  287 matrix multiplying the column vector  $\begin{bmatrix} u_q \\ v_q \end{bmatrix}$  equal to zero. The roots are 288

$$\omega_{\pm}^{2}(q) = \frac{K}{M_{1}M_{2}} \left\{ M_{1} + M_{2} \mp \left[ (M_{1} + M_{2})^{2} - 4M_{1}M_{2}\sin^{2}qa \right]^{1/2} \right\}.$$
(2.62)

We shall assume that  $M_1 < M_2$ . Then at  $q = \pm \frac{\pi}{2a}$ , the two roots are 290  $\omega_{\rm OP}^2(q = \frac{\pi}{2a}) = \frac{2K}{M_1}$  and  $\omega_{\rm AC}^2(q = \frac{\pi}{2a}) = \frac{2K}{M_2}$ . At  $q \approx 0$ , the two roots are 291 given by  $\omega_{\rm AC}^2(q) \simeq \frac{2Ka^2}{M_1+M_2}q^2$  and  $\omega_{\rm OP}^2(q) = \frac{2K(M_1+M_2)}{M_1M_2} \left[1 - \frac{M_1M_2}{(M_1+M_2)^2}q^2a^2\right]$ . 292 The dispersion relations for both modes are sketched in Fig. 2.8.

#### 2.5 Lattice Vibrations in Three Dimensions

Now let us consider a primitive unit cell in three dimensions defined by the 295 translation vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$ . We will apply periodic boundary conditions 296 such that  $N_i$  steps in the direction  $\mathbf{a}_i$  will return us to the original lattice site. 297 The Hamiltonian in the harmonic approximation can be written as 298

$$H = \sum_{i} \frac{\mathbf{P}_{i}^{2}}{2M} + \frac{1}{2} \sum_{i,j} \mathbf{u}_{i} \cdot \underline{C}_{ij} \cdot \mathbf{u}_{j}.$$
 (2.63) 299

294

Here, the tensor  $\underline{C}_{ij}$  (*i* and *j* refer to the *i*th and *j*th atoms and  $\underline{C}_{ij}$  is a 300 three-dimensional tensor for each value of *i* and *j*) is given by 301

$$\underline{C}_{ij} = \left[\nabla_{R_i} \nabla_{R_j} U(\mathbf{R}_1, \mathbf{R}_2, \ldots)\right]_{R_i^0 R_j^0}.$$
(2.64)