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Peter Brüesch

Phonons: Theory and Experiments I

Lattice Dynamics
and Models of Interatomic Forces

With 82 Figures

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Dr. Peter Brüesch

Brown Boveri Research Center, CH-5405 Baden-Dättwil, and
Ecole Polytechnique Fédéral de Lausanne, CH-1015 Lausanne, Switzerland

Series Editors:

Professor Dr. Manuel Cardona

Professor Dr. Peter Fulde

Professor Dr. Hans-Joachim Queisser

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1
D-7000 Stuttgart 80, Fed. Rep. of Germany

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Dedicated to my wife

Preface

This two-volume treatment grew out of lectures the author gave at the "Ecole Polytechnique Fédérale de Lausanne" during the years 1975-1980 for graduate students in experimental physics in their last year of study. It is written by an experimentalist with some interest in theory and is addressed mainly to experimentalists, but also to theoreticians interested in experiments. This treatment tries to bridge the gap between theory and experiments; it should assist experimentalists in the interpretation of their data in the vast field of lattice dynamics. An attempt has been made to provide not only the *basic concepts* but also a *working knowledge* in this field of solid-state physics.

In this first volume, the basic concepts of the physics of phonons are developed and illustrated by many examples; it provides the background necessary for the interpretation of most experimental results. The second volume, which is in preparation, is devoted to experimental techniques, the interpretation of experiments, and discussion of phenomena which are directly related with phonons.

The book is designed for introductory courses at the graduate level. It is believed that the book will also prove useful to those graduate students starting research in this or related fields, as well as to many workers already active in this branch of solid-state physics.

The author is indebted to BBC Brown, Boveri & Company Limited, Baden, Switzerland, for giving him the possibility to carry out this work. In particular, its Research Center provided the necessary scientific atmosphere to accomplish this goal. I am also grateful to the Ecole Polytechnique Fédéral de Lausanne for excusing me from my lecture duties during this period.

The entire manuscript was strongly influenced by the detailed criticism and valuable suggestions of my colleagues Drs. J. Bernasconi, H.U. Beyeler, T. Hibma, L. Pietronero, W.R. Schneider, S. Strässler, H.J. Wiesmann and H.R. Zeller from the Brown Boveri Research Center, and by Dr. W. Bührer

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Baden , December 1981

Peter Brüesch

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1. Introduction

1.1 The Static Lattice Model and Its Limitations

Many phenomena in solid-state physics can be understood on the basis of a static lattice model. In this model, the atoms of the solid are taken to constitute a fixed, rigid, immobile periodic array. Within this framework it is, for example, possible to account for a wealth of equilibrium properties of metals dominated by the behaviour of the conduction electrons. To some extent it is also possible to account for the equilibrium properties of ionic and molecular insulators.

The static lattice model is, of course, an approximation to the actual ionic configuration, because the atoms or ions are not fixed to their equilibrium positions, but rather oscillate about them with an energy which is governed by the temperature of the solid. The reason for these oscillations is due to the fact that the ions are not infinitely massive, nor are they held in place by infinitely strong forces. In classical theory the static lattice model can therefore be valid only at zero temperature. At nonzero temperatures, each ion must have some thermal energy and therefore a certain amount of motion in the vicinity of its equilibrium position. In quantum theory, even at zero temperature, the static lattice model is incorrect, because according to the uncertainty principle $\Delta x \Delta p \gtrsim \hbar$, localized ions possess some nonvanishing mean square momentum.

The dynamics of atoms in solids is responsible for many phenomena which cannot be explained within the static lattice model. Examples are the specific heat of crystals, thermal expansion, thermal conductivity, displacive ferroelectric phase transitions, piezoelectricity, melting, transmission of sound, certain optical and dielectric properties and certain aspects of the interaction of radiation such as X-rays and neutrons with crystals. The theory of lattice vibrations, often called *lattice dynamics*, and its implications for many of the above mentioned phenomena is the subject of this two-volume book.

1.2 Early History of Lattice Dynamics

The first example of lattice dynamics was the theory of the linear chain consisting of equidistant mass points with spring forces acting between them. This problem was the subject of many investigations in the eighteenth and nineteenth centuries. LAGRANGE in 1759 deduced the already known equations of motion for a continuous string by considering the string as the limit of the linear chain. It was CAUCHY in 1827 who first studied the dynamics of mass points located on a space lattice, assuming central forces to act between them. Based on this model, he deduced the corresponding continuum equations which contained at most 15 elastic constants; on the other hand, the most general equations for the motion of elastic bodies which CAUCHY had found somewhat earlier had 21 elastic constants. This resulted in 6 relations between the elastic constants which are known as the *Cauchy relations* and which are essentially a consequence of the assumption of central forces and certain symmetry properties (see Chap.3). The assumption of central forces is, in general, not valid in real crystals. In 1851, JELLET showed that many-body forces between the atoms leads to a violation of the Cauchy relations.

In 1819, DULONG and PETIT [1.1] published the results of their specific heat measurements of thirteen solid elements at room temperature. From these measurements, they deduced that the product of the specific heat and the atomic weight was approximately a constant: $C_V = 3R = 5.96 \text{ cal mole}^{-1}\text{K}^{-1}$. BOLTZMANN in 1871 demonstrated that the *law of Dulong and Petit* follows from his equipartition principle. However, in 1875, WEBER [1.2] found that the atomic specific heat of silicon, boron and carbon are considerably lower than the Dulong-Petit value. For example, the atomic specific heat of silicon, boron and diamond were found to be 4.8, 2.7, and $1.8 \text{ cal mole}^{-1}\text{K}^{-1}$, respectively, at room temperature. Subsequent specific heat measurements at $T < 300 \text{ K}$ revealed that the specific heat of solids decreased rapidly with decreasing temperature. Classical theory does not explain this behaviour.

In 1907, EINSTEIN [1.3] proposed a simple model to account for the decrease of the specific heat at low temperatures. He took the atoms of a crystal to be independent oscillators, each having the same frequency ω_E and able to vibrate isotropically. He then quantized the energy of the oscillators in accordance with the results obtained by PLANCK for radiation oscillators. The mean energy of a crystal of N_L atoms at temperature T is then given by

$$\bar{E} = \frac{3N_L \hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1} , \quad (1.1)$$

where k_B is Boltzmann's constant and N_L is Loschmidt's number. The atomic specific heat follows from

$$C_V = \left(\frac{d\bar{E}}{dT} \right)_V . \quad (1.2)$$

In Fig.1.1, C_V is shown as a function of T/θ_E where the *Einstein temperature* θ_E is an abbreviation for $\hbar\omega_E/k_B$; C_V is zero at $T = 0$ and rises asymptotically to the Dulong-Petit value $3R$ when $T \gg \theta_E$. For high temperatures, therefore, quantization is unimportant and the specific heat has the same value as if each degree of freedom of the system had energy $k_B T/2$; at lower temperatures, however, there is a pronounced deviation from the law of equipartition. According to PAIS [1.4], Fig.1.1 is the first graph dealing with the quantum theory of solids.

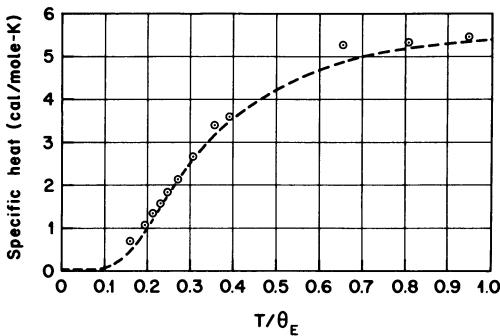


Fig.1.1. Comparison of experimental values of the heat capacity of diamond observed by WEBER [1.2] with values calculated by EINSTEIN [1.3] based on (1.1,2). For diamond, the Einstein temperature $\theta_E = \hbar\omega_E/k_B = 1320$ K

By these assumptions, EINSTEIN was able to explain the deviations from the Dulong-Petit law. But new measurements soon showed that EINSTEIN's theory was not satisfactory, particularly at low temperatures. In a later paper, EINSTEIN [1.5], therefore, studied the motion of an atom in a crystal considering its interactions with its neighbours and found that the assumption of a single vibrational frequency must be abandoned.

The idea of independently vibrating atoms had then already been questioned by MADELUNG [1.6] in a paper in 1909. In this study, the infrared vibrations of some alkali halides observed by RUBENS and coworkers [1.7] were, for the first time, regarded as *collective* vibrations where all the atoms in the lattice participate. MADELUNG chose, several years before the discovery of the

diffraction of X-rays by a crystal was published, the correct structure of the sodium chloride lattice and introduced noncentral force constants which freed him from the Cauchy relations. He was able to determine the force constants from the observed elastic constants and calculated the infrared vibration frequencies of these compounds. He was finally aware that in the infrared proper vibrations of long wavelength, the sodium and chloride lattices vibrate against each other.

The papers by EINSTEIN and MADELUNG stimulated DEBYE [1.8] and also BORN and VON KARMAN [1.9] in their research on lattice vibrations. Compared to EINSTEIN's theory of the specific heat, the fundamental advance made by DEBYE was the introduction of a frequency spectrum, each normal mode of which having the mean energy of a Planck oscillator as in the Einstein model. The difficult problem of finding the frequency distribution for a crystal lattice was drastically simplified by treating the normal modes of vibration as if they were waves in a continuous isotropic medium, instead of in a system in which the mass is concentrated at discrete points. This greatly simplifies the frequency distribution, and like EINSTEIN's theory, makes C_v the same function of T/θ_D for all crystals, where θ_D is the characteristic *Debye temperature* of a crystal (Fig.3.10). DEBYE's theory of specific heat was generally in excellent agreement with most of the experiment data. It was, in fact, not until 1930 that the deficiencies of DEBYE's theory began to be noticed in comparison with experimental results.

In 1912, BORN and VON KARMAN [1.9] introduced a more realistic model of lattice dynamics. The fundamental idea that each normal mode has the energy of a Planck oscillator was the same as DEBYE's, but the rest was completely different. They assumed that the atoms are arranged in a periodic three-dimensional array. The already known theory of the linear chain served as a guide but its generalization to three dimensions was not trivial. In such an array, the force on an atom depends not on its displacements from its equilibrium position but on its displacement relative to its neighbours. They introduced the periodic boundary conditions which greatly simplifies the calculations without affecting the bulk properties. The motion of the system turns out to be most readily described, not in terms of the vibrations of individual atoms but in terms of collective motions in the form of travelling waves called *lattice vibrations* by BORN. Each lattice vibration is characterized by a wave vector, a frequency and certain polarization properties. A quantized lattice vibration or normal mode is called a *phonon* which has "particle-like" properties, in analogy with the photon, which is a quantized elec-

tromagnetic wave. The analysis leads to the notion of acoustic and optic phonon branches, to a generalized Debye model for the specific heat, the limit of long waves and the passage to the continuum description.

The theory of the influence of thermal motion on the scattering of X-rays on crystals was first studied by DEBYE [1.10] and by WALLER [1.11]. The thermal motion of the atoms causes a decrease in the intensity of the *Bragg reflections* with increasing temperature. The part of intensity lost from the main beam appears as "diffusely scattered" radiation which is observed in directions not allowed by *Bragg's law*. Experimentally, this thermal diffuse scattering was first detected by LAVAL [1.12] in 1938 and correctly explained by him in terms of the *Born-von Karman theory*. Continuing this research, OLMER [1.13] in 1948 and WALKER [1.14] in 1956 deduced dispersion curves for aluminium. This technique has also been applied by other workers to obtain the dispersion curves of iron, copper and zinc. A comprehensive theoretical investigation on the relationship between crystal dynamics and X-ray scattering was given by BORN [1.15] in 1942.

Electromagnetic waves with wavelengths from the visible to the infrared region can interact in various ways with lattice vibrations. These long wavelength lattice vibrations which produce an oscillating dipole moment interact strongly with light in the infrared and far-infrared regions and lead to absorption and reflection bands in narrow frequency regions. Such experiments were first performed by RUBENS [1.7] in 1910 and by BARNES [1.16] in 1932. The wavelengths corresponding to the absorption frequencies are also known as residual rays or, from the German, Reststrahl wavelengths.

Light in the visible region is scattered by both acoustic sound waves and by certain optical phonons. In 1914 and 1922, BRILLOUIN [1.17] calculated the spectrum of light scattered by density fluctuations associated with sound waves. He found that the spectrum consists of a doublet split symmetrically around the frequency of the incident light. The splitting, which is very much smaller than the frequency of the incident light, is determined by the velocity of those sound waves whose wavelength is close to that of the light. The Brillouin doublets were first observed by GROSS [1.18] between 1930 and 1932 in liquid media. This experimental technique is now known as *Brillouin scattering*.

In 1923, SMEKAL [1.19] studied the scattering of light by a system with two quantized energy levels and predicted the existence of sidebands in the spectrum. This effect was subsequently observed by RAMAN and KRISHNAN [1.20] in 1928; they found that light scattered by liquids contains sharp sidebands

symmetrically disposed around the incident frequency with shifts identical to the frequencies of some of the infrared vibrational absorption bands. Simultaneously, LANDSBERG and MANDELSTAM [1.21] discovered a similar phenomenon in quartz. This inelastic scattering of light by molecular and crystal vibrations is known as the *Raman effect*. It is caused by those long wavelength optical phonons which modulate the electronic polarizability of the system. The vibrational Raman effect was studied theoretically in detail by PLACZEK [1.22] in 1934.

In 1954, BORN and HUANG published their well-known book "*The Dynamical Theory of Crystal Lattices*" which is still an authoritative work on many aspects of the subject.

Shortly afterwards, PLACZEK and VAN HOVE [1.23] investigated the possibility of using inelastic scattering of thermal neutrons to study lattice vibrations. BROCKHOUSE [1.24] followed this suggestion in 1955 and got the first dispersion curves for lattice vibrations in aluminium. Inelastic scattering of neutrons is now the most important technique for studying phonons. The reason is that in contrast to X-rays, neutrons which have come into thermal equilibrium with matter at about room temperature have energies of the same order of magnitude as phonons. The wavelength associated with a beam of monochromatic neutrons in this range is of the same order of magnitude as interatomic distances and the beam will be diffracted by a crystal. As in the case of X-rays, there is again elastic scattering according to Bragg's law. The neutron beam is, however, also diffracted in other directions by travelling waves and exchanges energy with them in units of the phonon energy, which is directly proportional to the frequency. Consequently, by measuring the change in direction and in energy of the scattered neutrons, it is possible to obtain the whole phonon spectrum, i.e., the phonon frequencies as a function of wave vectors for all the acoustic and optic branches. This new technique opened the possibility of obtaining detailed information about the interatomic forces and marked a new era in lattice dynamics.

1.3 The Adiabatic and Harmonic Approximations

So far we have regarded the atoms merely as point masses with no structure. In reality we are, of course, dealing with nuclei and electrons, and the question arises to which extent the motion of the nuclei are independent of the motion of the electrons. The "core" electrons no doubt move rigidly with

the nuclei in the course of lattice vibrations, but the wave functions of the valence electrons do not remain unaffected. Consequently, we usually consider the ion cores and the valence electrons as independent constituents of the solid. It is not, however, always possible to make such a clear distinction, and herein lies the first approximation. Let us briefly consider the vastly more complex problems which arise when we attempt to treat the crystal in a more fundamental way, namely, in terms of the constituent ions and valence electrons. The problem may be clarified by means of the BORN-OPPENHEIMER argument which leads to what is known as the *adiabatic approximation* [1.25]. The essential idea is that the ions being about 2×10^3 to 10^5 times heavier, move much more slowly than the electrons. At any given instant, therefore, the electrons "see" the ions fixed in some (in general, displaced) configuration. During the ionic motion the electrons move as though the ions were fixed in their instantaneous positions. We say that the electrons follow the ionic motion *adiabatically*. In an adiabatic motion, an electron does not make abrupt transitions from one state to others; instead, an electronic state itself is deformed progressively by the ionic displacements.

In the following, we briefly sketch some formal expressions of the main results of the adiabatic approximation. For a detailed discussion the reader is referred to [1.25-33]. We start with the total Hamiltonian for the crystal, using r as a collective symbol for the coordinates of the valence electrons and R similarly for the ionic coordinates. Thus we write

$$H = T_e + T_i + \Phi_{ii}(R) + \Phi_{ee}(r) + \Phi_{ie}(r, R) , \quad (1.3)$$

the subscripts i and e denoting ions and valence electrons. T_e and T_i are the kinetic energy operators of the electrons and ions, $\Phi_{ee}(r)$ and $\Phi_{ii}(R)$ are the electron-electron and direct ion-ion interactions, respectively, while $\Phi_{ie}(r, R)$ is the electron-ion interaction. Let $\Xi(r, R)$ be the eigenfunction of the Hamiltonian (1.3), so that

$$H \Xi(r, R) = E \Xi(r, R) , \quad (1.4)$$

where E is the total energy of the entire system. In the adiabatic approximation, we imagine the ions to be *fixed* in some configuration and for this particular R we can construct the Schrödinger equation for the electrons

$$[T_e + \Phi_{ee}(r) + \Phi_{ie}(r, R)]x_R(r) = E_e(R)x_R(r) . \quad (1.5)$$

Here $x_R(r)$ is a wave function for the entire system of electrons; $x_R(r)$ is a function of all variables represented by r and contains the ionic coordinates R as parameters. Likewise, the electronic energy $E_e(R)$ depends on the

ionic coordinates. Note that $E_e(R)$ is not just a potential energy; it includes not only the electron-electron and ion-electron interactions but also the kinetic energy of the electronic motion which automatically changes as the coordinates R are changed. Let us try the following Ansatz for $\Xi(r,R)$

$$\Xi(r,R) = \chi_R(r)\psi(R) . \quad (1.6)$$

Substituting (1.6) in (1.4) and making use of (1.5), it may be shown that (1.6) is indeed a solution of (1.4), provided certain terms can be neglected and the ionic wave function $\psi(R)$ is chosen to satisfy (Problem 1.5.1)

$$[T_i + \Phi_{ii}(R) + E_e(R)]\psi(R) = E\psi(R) . \quad (1.7)$$

An elementary discussion of the neglected terms is given in [1.32]. Equation (1.8) is an equation for a wave function of the ions alone. The essential point is that for the ionic motion, an *effective potential energy function*

$$\Phi(R) = \Phi_{ii}(R) + E_e(R) \quad (1.8)$$

has been introduced, to which the electrons contribute through $E_e(R)$. $\Phi(R)$ can be used as a potential energy for discussing the motion of the ions.

To illustrate the adiabatic approximation, we consider the H_2^+ molecule in its electronic ground state [1.34]. This molecule consists of two protons separated by a distance R and of one electron (Fig.1.2). In this case, $\Phi_{ii}(R) = e^2/R$ is the repulsive energy between the protons, while $E_e(R)$ represents the attractive energy which arises indirectly through the presence of the electron which "glues" the two protons together. $E_e(R)$ can be calculated from (1.5); since there is only one electron, we have $\Phi_{ee}(r) = 0$ and $\Phi_{ie}(r,R) = -(e^2/r_a) - (e^2/r_b)$, where r_a and r_b are the distances between the electron and the two protons a and b. The functions $\Phi_{ii}(R)$, $E_e(R)$ and $\Phi(R)$ are shown in Fig.1.2. We see that $\Phi(R)$ has a minimum at about $R_0 = 2a_0$ ($a_0 = 0.529 \text{ \AA}$) and therefore represents a stable state of the molecule.

The validity of the adiabatic approximation for lattice dynamics has been discussed by several authors [1.27-33]. The main result is that the approximation is valid for the lattice dynamics of insulators as well as of semiconductors and metals. In insulators and large gap semiconductors, the approximation is valid because the excited states of the electrons are separated from the ground state by energies large compared with phonon energies $\hbar\omega$. This is certainly not the case in small gap semiconductors and metals. Indeed, in the vicinity of the Fermi surface of a metal, electronic transitions are possible with arbitrary small excitation energies and for electrons with energies within $\hbar\omega$ of the *Fermi energy* E_F , the above-mentioned abrupt transitions

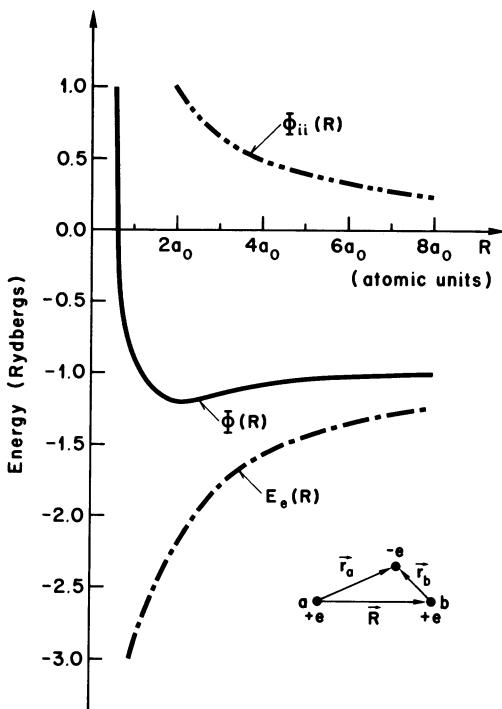


Fig. 1.2. Electronic energy $E_e(R)$, internuclear repulsive energy $\Phi_{ii}(R)$ and total energy $\Phi(R)$ as a function of interatomic distance R for the ground state of the hydrogen molecule-ion, H_2^+ , shown in the inset

associated with the motion of the ions cannot be completely excluded. However, the number of electrons in this thin "thermal layer" of thickness $\hbar\omega$ is very small compared with the total number of electrons in the conduction band. For the latter the excitation energy is of the order of E_F , and therefore they must follow the vibrating ions adiabatically. It can indeed be shown [1.27-29] that in metals the residual electron-ion interaction contained in the terms neglected in the adiabatic approximation (Problem 1.1) contribute to the phonon frequencies of metals of the order of $\Delta\omega = \omega(\hbar\omega_0/E_F)$, where ω_0 is a typical phonon frequency. Since E_F is of the order of several eV and $\hbar\omega_0$ of the order of 0.01 - 0.1 eV, the ratio $\hbar\omega_0/E_F$ is about 10^{-3} to 10^{-2} and for this reason the adiabatic approximation is also quite accurate for the lattice dynamics of metals.

The adiabatic approximation can even be used for the lattice dynamics of metals with strong electron-phonon interaction which is responsible for such phenomena as the *Kohn anomaly* (Chap. 4) and the *Peierls distortion* [1.35]. The relevant static effects of the electron-phonon interaction are already contained in the electronic energy $E_e(R)$ appearing in (1.7) because this energy depends on the electron-ion interaction $\Phi_{ie}(R)$, as can be seen from (1.5).

Thus, in the rest of this book we will assume the validity of the adiabatic approximation. It should be mentioned, however, that the adiabatic approximation breaks down for phenomena where the dynamics of the electrons are directly involved such as the resistance due to scattering of electrons by phonons and superconductivity.

The adiabatic approximation makes it possible to work with an *effective* potential $\Phi(R)$ given by (1.8) if we are dealing with the motion of the ions. The evaluation of $E_e(R)$ on the basis of (1.5), however, is a very difficult problem in general. A more practical approach is to assume some *phenomenological potential* for $\Phi(R)$ which contains only a few parameters. For the diatomic molecule, for example, a good choice is the Morse potential given by (5.1). Phenomenological potentials for atoms in solids are discussed in Chap.4.

In general, the effective potential $\Phi(R)$ depends on all the individual coordinates R_ℓ of the ions: $\Phi(R) = \Phi(\dots R_\ell \dots R_k \dots)$. If the displacements of the ions from their equilibrium positions $R_{\ell 0}$ are small, $\Phi(R)$ can be written as a power series in the displacements $u_\ell = R_\ell - R_{\ell 0}$:

$$\Phi(\dots R_\ell \dots R_k \dots) = \Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 + \dots$$

$$\begin{aligned} &= \Phi(\dots R_{\ell 0} \dots R_{k 0} \dots) + \sum_\ell f_\ell u_\ell + \frac{1}{2} \sum_{\ell k} f_{\ell k} u_\ell u_k \\ &\quad + \frac{1}{3!} \sum_{\ell km} f_{\ell km} u_\ell u_k u_m + \frac{1}{4!} \sum_{\ell k mn} f_{\ell k m n} u_\ell u_k u_m u_n + \dots . \end{aligned} \quad (1.9)$$

Here, $f_{\ell k}$, $f_{\ell km}$ etc. are the expansion coefficients or force constants. In the *harmonic approximation*, the series is terminated at Φ_2 . (For the harmonic vibration of a diatomic molecule see Problem 1.5.2).

As will be discussed in Chap.3, in the harmonic approximation the force on an atom is strictly proportional to its displacement relative to its neighbours, which is nothing other than *Hook's law*. The harmonic approximation is the starting point for all theories of lattice dynamics. Further corrections to $\Phi(R)$, especially those of Φ_3 and Φ_4 , are known as *anharmonic terms*. The theory of lattice dynamics is much more complicated if anharmonic effects are considered. The additional terms in Φ_3 and Φ_4 can often be treated as a perturbation and are essential for a discussion of such properties as thermal expansion and thermal conductivity. Anharmonicity leads to interactions between different normal modes; in the particle picture this leads to collisions between the phonons. The pioneering work in the field of anharmonicity is due to BORN [1.36] and DEBYE [1.37] in 1914, GRÜNEISEN [1.38] in 1926, PEIERLS

[1.39] in 1929, BORN and BLACKMAN [1.40] in 1933, BORN [1.41] in 1951 and HOOTON [1.42] in 1958. Anharmonic effects will be discussed in Chap.5.

1.4 Organization of the Book

This text of the two-volume treatment contains most of the theoretical background necessary to understand experiments in the field of phonons. This background is presented in four basic chapters. Chapter 2 starts with the diatomic linear chain. In the classical theory we discuss the periodic boundary conditions, equation of motion, dynamical matrix, eigenvalues and eigenvectors, acoustic and optic branches and normal coordinates. The transition to quantum mechanics is achieved by introducing the *Schrödinger equation* of the vibrating chain. This is followed by the occupation number representation and a detailed discussion of the concept of phonons. The chapter ends with a discussion of the specific heat and the density of states.

In Chap.3, the theory is generalized to three-dimensional crystals with a basis. Chapter 3 also contains a section dealing with the connection of lattice dynamics and the theory of elasticity. The force constants, dynamical matrix and dispersion relation are illustrated with the help of monoatomic crystals with fcc structure.

While in Chaps.2 and 3 a straightforward formalism is developed, the philosophy in Chap.4 is different; in this chapter we are concerned with an interpretation of measured phonon dispersion curves and the information they provide for the interatomic forces. It is an important chapter and certainly not an easy one; the difficulties are intrinsic and arise from the complicated nature of the different types of chemical bonds. The chapter contains the study of the lattice dynamics of solid inert gases, ionic crystals, covalent solids, molecular crystals and a qualitative discussion of the lattice dynamics of metals.

In Chap.5, anharmonic effects are considered. After an illustration of anharmonicity with the help of the diatomic molecule, we derive the free energy of the anharmonic linear chain and discuss the equation of state and the specific heat. The "quasi-harmonic approximation" worked out in detail for the linear chain is then applied to three-dimensional crystals to obtain the equation of state and thermal expansion. The "self-consistent harmonic approximation" is the basis for treating the effects of strong anharmonicity. At the end of this chapter we give a qualitative discussion of the response

function for systems with weak anharmonicity, as well as of frequency widths and shifts.

I have tried to present both aspects of the subject, descriptive and analytical. The power of simple models to illustrate basic concepts should not be underestimated. Simple models such as simple three-dimensional lattices, the linear chain and even the diatomic molecule are studied at various places in this book. Many figures are included to illustrate both theoretical and experimental results. The interested reader will find all lengthy derivations in an Appendix; the basic physical ideas can be understood without the Appendix, but for a deeper understanding of many aspects its content will be helpful. Each chapter contains a number of problems with hints and results. They not only help the reader to exercise newly acquired skills but also contain additional information not contained in the text. It is therefore recommended that readers examine the problems, even if they do not intend to solve them. At the end of each chapter, references to existing literature appear. Despite the inclusion of over 200 references, it is easily possible that I have omitted important papers. If this is the case, it is unintentional and apologies are sincerely offered.

I have to say a word about the notation. It is the same as that used in other books about this subject. This notation might sometimes look complicated. The basic concepts (linear oscillator, Hook's law, etc.) are simple but the lattice with a basis introduces an unavoidable complex notation. Experience has shown, however, that students become accustomed to the notation very quickly. Therefore, there is no reason to be discouraged by this. Whenever possible I have tried to use a simpler or condensed notation. Appendix Q contains the most important physical constants and units used in this book.

While the present first volume contains much of the theoretical background, the emphasis in [1.35] is on experimental techniques, the interpretation of experimental results and the discussion of a number of phenomena which are directly related to phonons. Correspondingly, the second volume will contain a number of rather short chapters and its style will be somewhat different from this volume by exchanging depth for breadth in many places. It is planned to introduce the reader into the following topics: Infrared, Raman and Brillouin spectroscopy, interaction of X-rays with phonons, inelastic neutron scattering and some other techniques of interest. Phenomena such as piezoelectricity, ferroelectricity, melting and thermal conductivity will be given a qualitative discussion. The book will also contain some newer developments;

in particular, one-dimensional metals and superionic conductors. Furthermore, a qualitative discussion of phonons in disordered systems and solitons is planned.

1.5 Problems

1.5.1 Adiabatic Approximation

Using (1.3-6) show that (1.7) is obtained, provided that the terms

$$-\sum_{\ell} \frac{\hbar^2}{2M_{\ell}} \left[2 \frac{\partial \psi(R)}{\partial R_{\ell}} \frac{\partial x_R(r)}{\partial R_{\ell}} + \psi(R) \frac{\partial^2 x_R(r)}{\partial R_{\ell}^2} \right],$$

can be neglected.

Hint: Write the kinetic energy operator of the ions in the form

$$T_i = -\sum_{\ell} \frac{\hbar^2}{2M_{\ell}} \frac{\partial^2}{\partial R_{\ell}^2},$$

where M_{ℓ} is the mass of ion ℓ and R_{ℓ} denotes its position. Calculate $T_i x_R(r) \psi(R)$ by partial differentiation.

The first sum in the neglected terms quoted above is responsible for the scattering of electrons by the thermal vibrations, giving rise to resistance to electronic transport [1.33].

1.5.2 Harmonic Vibration of a Diatomic Molecule

Consider a diatomic molecule with masses m_1 and m_2 and interatomic distance R . Let r_1 and r_2 be the distances of m_1 and m_2 from the center of mass. Expanding the effective potential $\phi(R)$ in the form

$$\phi(R) = \phi(R_0) + \frac{k}{2} (R - R_0)^2 + \dots,$$

where R_0 is the distance at the minimum of $\phi(R)$, show that in the harmonic approximation the vibrational frequency is given by

$$\omega = (k/\mu)^{1/2},$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass and k is the force constant [curvature of $\phi(R)$ at $R = R_0$].

Hint: Use $r_1 + r_2 = R$, $m_1 r_1 = m_2 r_2$, and $m_1 \ddot{r}_1 = -d\phi(R)/dR$.

2. Dynamics of the Linear Diatomic Chain

In this chapter, we start with the classical mechanics of the linear diatomic chain with nearest-neighbour interactions. Using periodic boundary conditions the equations of motion are solved and the dispersion relations are discussed. We also discuss the transition from the diatomic chain to the monoatomic chain.

The model of the diatomic chain is well suited to discussing the dynamical matrix and eigenvectors. We then introduce normal coordinates in terms of which the vibrations of the diatomic chain can be decomposed into a system of independent harmonic oscillators. Quantization of this system is achieved either by expressing the Hamilton function in terms of real normal coordinates and formulating the corresponding Schrödinger equation or by introducing creation and annihilation operators. The concept of phonons or quantized lattice vibrations is discussed. Finally, we introduce the frequency distribution or density of states and calculate the specific heat of the diatomic linear chain using the Debye and Einstein approximations.

It should be emphasized that some of the results derived in this chapter can also be formally applied to simple three-dimensional crystals such as the alkali halides. If in such crystals elastic waves are propagating in directions of high symmetry, for instance, parallel to the (111)-direction in NaCl or parallel to the (100)-direction in CsCl, entire planes containing only one kind of ion vibrate against each other so that the problem becomes one-dimensional and can be formally treated with the model of the diatomic chain.

This chapter is an important one because it contains already most of the essential concepts of the dynamics of atoms in crystals. Many of the essential features of the diatomic chain will also apply to the three-dimensional case. This justifies a somewhat detailed derivation of the results obtained in this chapter. In addition, we introduce here the notation used for the dynamics of general three-dimensional crystals treated in Chap.3.

2.1 Classical Mechanics

2.1.1 Periodic Boundary Conditions and Dispersion Relations

We begin with the linear chain with two atoms of masses m_1 and m_2 per unit cell of dimension a (Fig.2.1).

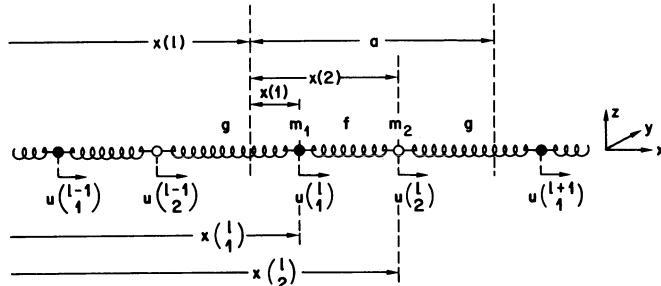


Fig.2.1. Diatomic linear chain with masses m_1 and m_2 and nearest-neighbour interactions with force constants f and g . $u_{\kappa}^{(\ell)}$ is the displacement of atom κ in unit cell ℓ from its equilibrium position $x_{\kappa}^{(\ell)}$

Each atom has three degrees of freedom corresponding to small displacements in the x , y , and z -directions (Fig.2.1). The restoring forces opposing these displacements can, in principle, be calculated if the interaction energy between the atoms as a function of their coordinates is known; this will be discussed in Chap.4. In general, smaller restoring forces and hence smaller force constants are obtained for displacements perpendicular to the chain than for displacements parallel to the chain. We assume here for simplicity that the forces between the atoms extend to nearest neighbours only and that these forces are harmonic in the sense as discussed in Chap.1. In Fig.2.1, the harmonic forces opposing displacements in the x -direction are represented symbolically by massless springs of force constants f and g . These force constants are regarded as phenomenological parameters. For the time being we consider only *longitudinal vibrations* with displacements parallel to the x -direction, which is the direction of propagation of the wave. *Transverse vibrations* with displacements perpendicular to the x -direction can be treated similarly, but the corresponding frequencies are, in general, smaller than those for the longitudinal vibrations.

The chain considered contains N unit cells numbered by an index $\ell = 1, \dots, N$. In each unit cell the masses are numbered by an index $\kappa = 1, 2$ and their equilibrium positions in each cell are x_{κ} . We could of course choose the origin

to make $x(1) = 0$ if we wished. The equilibrium position of atom κ in unit cell ℓ with lattice parameter a is

$$x(\ell_\kappa) = x(\ell) + x(\kappa) = \ell a + x(\kappa) \quad (2.1)$$

and as a result of thermal fluctuations, the displacement of this atom from its equilibrium position is $u(\ell_\kappa)$ (Fig. 2.1).

In order to define the problem completely it is necessary to specify the boundary conditions, that is, to specify how the atoms at the ends of the chain are to be described. Various boundary conditions are clearly possible, for instance, fixed or free-end conditions. Free-end conditions would correspond to the physically most realistic situation. In real crystals, the behaviour of the atoms at and near the surface is of crucial importance for many *surface* properties, but the mathematical treatment of the boundary conditions for particles interacting at large distances is very complex [2.1, 2]. It can, however, be shown mathematically [2.3], and is indeed intuitively obvious, that the calculation of *bulk* properties such as the specific heat are not influenced by the choice of the boundary conditions as long as N is sufficiently large that atoms at the end of the chain comprise a negligible fraction of the total. We therefore choose the boundary conditions on grounds of mathematical convenience. By far the most convenient choice is the *cyclic boundary condition*: in the linear chain of Fig. 2.1, we simply join the remote ends of the chain back together by one more spring of force constant g and obtain $2N$ atoms constrained to remain on a circular ring as shown in Fig. 2.2 for $N = 4$.

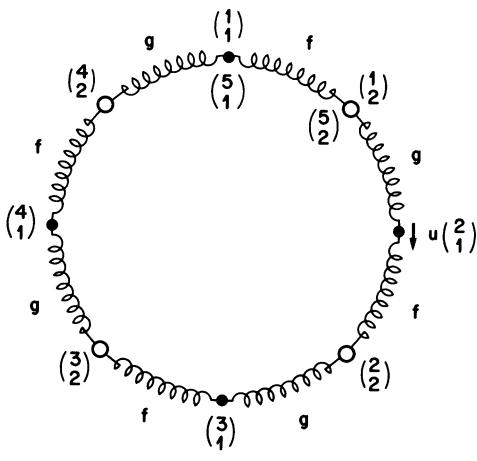


Fig. 2.2. Periodic or cyclic boundary conditions for a linear diatomic chain with $N = 4$ unit cells. The atoms are numbered as (ℓ_κ) where ℓ is the unit cell and $\kappa = 1, 2$ numbers the atom in the unit cell. The condition for the displacements is $u(\ell+4)_\kappa = u(\ell)_\kappa$

In Fig.2.2, the periodic boundary conditions are $u(1) = u(5)$ or $u(2) = u(6)$, etc., or more generally we require that

$$u(\frac{\ell+N}{\kappa}) = u(\frac{\ell}{\kappa}) \quad (2.2)$$

for all atoms $(\frac{\ell}{\kappa})$. Instead of considering the atoms constrained to remain on a circular ring, it is also possible to regard our one-dimensional crystal with $2N$ atoms as part of an infinite chain (Fig.2.3). We are then not troubled by end effects because all lattice points are equivalent, but we require that the displacements of atom $(\frac{\ell}{\kappa})$ is the same as that of atom $(\frac{\ell+N}{\kappa})$ for all the $2N$ atoms of the crystal considered. Thus, the periodic boundary condition postulates that the atomic displacements be periodic with the length Na of the crystal. In contrast to the ring-picture of Fig.2.2, the latter picture can easily be extended to two and three dimensions. In this form we are dealing with the Born-von Karman or periodic boundary conditions.

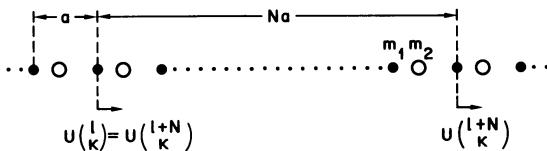


Fig.2.3. Born-von Karman or periodic boundary conditions. The linear chain we are studying contains N unit cells with lattice parameter a and is part of an infinite chain. For the displacements we require that $u(\frac{\ell+N}{\kappa}) = u(\frac{\ell}{\kappa})$

The Hamiltonian of the system is the sum of the kinetic energy T and the potential energy Φ

$$H = T + \Phi \\ = \sum_{\ell \kappa} \frac{p^2(\frac{\ell}{\kappa})}{2m_{\kappa}} + \frac{1}{2} \sum_{\ell} \left\{ f[u(\frac{\ell}{2}) - u(\frac{\ell}{1})]^2 + g[u(\frac{\ell+1}{1}) - u(\frac{\ell}{2})]^2 \right\} \quad (2.3)$$

where

$$p(\frac{\ell}{\kappa}) = m_{\kappa} \dot{u}(\frac{\ell}{\kappa}) \quad (2.4)$$

is the momentum of atom $(\frac{\ell}{\kappa})$.

The equations of motion are obtained by calculating the force $-\partial\Phi/\partial u(\frac{\ell}{\kappa})$ acting on the atom $(\frac{\ell}{\kappa})$:

$$m_{\kappa} \ddot{u}(\frac{\ell}{\kappa}) = - \frac{\partial \Phi}{\partial u(\frac{\ell}{\kappa})} . \quad (2.5)$$

With ϕ given by (2.3), we immediately obtain

$$\begin{aligned} m_1 \ddot{u}_{(1)}^{\ell} &= f[u_{(2)}^{\ell} - u_{(1)}^{\ell}] + g[u_{(2)}^{\ell-1} - u_{(1)}^{\ell}] \\ m_2 \ddot{u}_{(2)}^{\ell} &= g[u_{(1)}^{\ell+1} - u_{(2)}^{\ell}] + f[u_{(1)}^{\ell} - u_{(2)}^{\ell}] \quad . \end{aligned} \quad (2.6)$$

We consider a solution of the following form [2.4]:

$$u_{(\kappa)}^{\ell} = (Nm_{\kappa})^{-\frac{1}{2}} |A(q)| |e(\kappa|q)| \cos[\beta(\kappa|q)] \quad , \quad (2.7a)$$

where the phase is

$$\beta(\kappa|q) = qx_{(\kappa)}^{\ell} - \omega(q)t + \alpha(q) + \varphi(\kappa|q) \quad . \quad (2.8)$$

If $q > 0$, (2.7a) with (2.8) represents a wave travelling to the right and describes the undamped propagation of a disturbance through the chain.

$(Nm_{\kappa})^{-\frac{1}{2}}$ is a normalizing factor, $|A(q)|$ and $|e(\kappa|q)|$ are real amplitudes, $q = 2\pi/\lambda$ is the wave number (λ the wavelength), $\omega(q)$ the angular frequency and $\alpha(q)$ and $\varphi(\kappa|q)$ are phases. Note that the quantity qa is the change in phase in passing from the atom (κ) to the atom $(\kappa+1)$, which are a distance a apart. The amplitude $|A(q)|$ and the phase $\alpha(q)$ are determined by the initial conditions but we shall find that the amplitude $|e(\kappa|q)|$ and the phase $\varphi(\kappa|q)$ will be determined by the equations of motion (2.6). For this reason, both the total amplitude and its phase have been divided into two independent parts [2.4]. For convenience we represent the travelling wave (2.7a) by exponentials. Using $\cos\beta = (1/2)[\exp(i\beta) + \exp(-i\beta)]$ we can write

$$u_{(\kappa)}^{\ell} = \frac{1}{2} (Nm_{\kappa})^{-\frac{1}{2}} (A(q)e(\kappa|q)\exp[i[qx_{(\kappa)}^{\ell} - \omega(q)t]] + c.c.) \quad , \quad (2.7b)$$

where

$$A(q) = |A(q)| e^{i\alpha(q)} \quad (2.9)$$

$$e(\kappa|q) = |e(\kappa|q)| e^{i\varphi(\kappa|q)} \quad (2.10)$$

and c.c means the conjugate complex expression of the first term in the large brackets of (2.7b). Substituting this assumed solution in (2.6), one finds after separating out terms which have the same time dependence and cancellation of common factors

$$\begin{aligned} D_{11}(q)e(1|q) + D_{12}(q)e(2|q) &= \omega^2(q)e(1|q) \\ D_{21}(q)e(1|q) + D_{22}(q)e(2|q) &= \omega^2(q)e(2|q) \quad . \end{aligned} \quad (2.11)$$

In (2.11) we have used the following abbreviations:

$$\begin{aligned} D_{11}(q) &= \frac{f+g}{m_1} & D_{22}(q) &= \frac{f+g}{m_2} \\ D_{12}(q) = D_{21}^*(q) &= -(m_1 m_2)^{-\frac{1}{2}} e^{iq(x_2 - x_1)} (f + g e^{-iqa}) \end{aligned} \quad (2.12)$$

and we have replaced $x(\kappa)$ by the simpler notation x_κ .

The condition that the linear and homogeneous system (2.11) has a non-trivial solution for the amplitudes $e(\kappa|q)$ is that its determinant vanishes [2.5]:

$$\begin{vmatrix} D_{11}(q) - \omega^2(q) & D_{12}(q) \\ D_{21}(q) & D_{22}(1) - \omega^2(q) \end{vmatrix} = 0 \quad . \quad (2.13)$$

Solving (2.13), we obtain the following *dispersion relation* for the *eigenvalues* $\lambda_{1,2}(q)$ or the *eigenfrequencies* $\omega_{1,2}(q)$:

$$\lambda_{1,2}(q) = \omega_{1,2}^2(q) = \frac{f+g}{2\mu} \left[1 \pm \left(1 - \frac{16fg}{(f+g)^2} \frac{\mu^2}{m_1 m_2} \sin^2 \frac{aq}{2} \right)^{\frac{1}{2}} \right] \quad (2.14)$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (2.15)$$

is the *reduced mass*. There are two branches, a longitudinal-acoustic branch (LA) defined by $\omega_1(q)$ [- sign in (2.14)] and a longitudinal-optic branch (LO) [+ sign in (2.14)]. Similar results are obtained for the transverse-acoustic branches (TA) and the transverse-optic branches (TO) but with different force constants. The name acoustic branch is due to the fact that if the wavelength λ is large compared with the lattice spacing a ($aq \ll 1$), a disturbance of this sort propagates like a *sound wave* in an *elastic continuum*. On the other hand, the name optic branch comes from the fact that the modes with frequencies $\omega_2(q \rightarrow 0)$ can often be excited by electromagnetic fields in the infrared or far-infrared region [1.35].

2.1.2 Dynamical Matrix and Eigenvectors

In the following, we confine ourselves to the longitudinal branches LA and LO which we number by an index $j = 1, 2$. The treatment of the transverse vibrations TA and TO is completely analogous. If we substitute one of the eigen-

values $\omega_j^2(q)$ given by (2.14) in (2.11), we obtain amplitudes $e(\kappa|_j^q)$ belonging to $\omega_j^2(q)$. Therefore, we have

$$\begin{aligned} D_{11}(q)e(1|_j^q) + D_{12}(q)e(2|_j^q) &= \omega_j^2(q)e(1|_j^q) \\ D_{21}(q)e(1|_j^q) + D_{22}(q)e(2|_j^q) &= \omega_j^2(q)e(2|_j^q) . \end{aligned} \quad (2.16)$$

In matrix notation we can write [2.5]

$$D(q)e(q) = e(q)\Lambda(q) . \quad (2.17)$$

The matrix

$$D(q) = \begin{pmatrix} D_{11}(q) & D_{12}(q) \\ D_{21}(q) & D_{22}(q) \end{pmatrix} \quad (2.18)$$

with elements given by (2.12) is called the *dynamical matrix*. $\Lambda(q)$ is the following diagonal eigenvalue matrix

$$\Lambda(q) = \begin{pmatrix} \omega_1^2(q) & 0 \\ 0 & \omega_2^2(q) \end{pmatrix} , \quad (2.19)$$

while the *eigenvector matrix* $e(q)$ is given by

$$e(q) = \begin{pmatrix} e(1|_1^q) & e(1|_2^q) \\ e(2|_1^q) & e(2|_2^q) \end{pmatrix} . \quad (2.20)$$

According to (2.12), $D_{21}^*(q) = D_{12}(q)$, that is, $D(q)$ is a *Hermitian matrix*:

$$D^+(q) = D^{*T}(q) = D(q) , \quad (2.21)$$

where D^{*T} is the transposed and complex conjugate matrix of D .

Defining *eigenvectors* [columns of $e(q)$]

$$\vec{e}_j^q = \begin{pmatrix} e(1|_j^q) \\ e(2|_j^q) \end{pmatrix} , \quad (2.22)$$

Equation (2.17) can also be written in the form

$$D(q)\vec{e}_j^q = \omega_j^2(q)\vec{e}_j^q . \quad (2.23)$$

The homogeneous equations (2.16) or (2.17) define the matrix $e(q)$ to within a constant factor only. On the other hand, $e(q)$ diagonalizes the Hermitian matrix $D(q)$: $e^{-1}(q)D(q)e(q) = \Lambda(q)$. Therefore, $e(q)$ can be chosen to be a unitary matrix which fixes the undetermined factor. Thus, we require $e^{-1}(q) = e^{*\dagger}(q)$ or

$$e^+(q)e(q) = e(q)e^+(q) = I , \quad (2.24)$$

where I is the unit matrix. Since the rows and the columns of a unitary matrix are orthogonal, we have the following orthonormality and closure conditions:

$$\sum_{\kappa} e^*(\kappa|_j^q) e(\kappa|_j^q) = \delta_{jj}, \quad (2.25)$$

$$\sum_j e(\kappa|_j^q) e^*(\kappa'|_j^q) = \delta_{\kappa\kappa'} . \quad (2.26)$$

From (2.12) it follows that

$$D(-q) = D^*(q) \quad (2.27)$$

and from (2.14,19) we obtain

$$\Lambda(-q) = \Lambda(q) . \quad (2.28)$$

Replacing q by $-q$ in (2.17) and using (2.27,28) gives

$$D^*(q)e(-q) = e(-q)\Lambda(q) . \quad (2.29a)$$

Forming the complex conjugate of (2.29a) and remembering that the eigenvalues of a Hermitian matrix are real, i.e., $\Lambda^*(q) = \Lambda(q)$, one obtains

$$D(q)e^*(-q) = e^*(-q)\Lambda(q) . \quad (2.29b)$$

Comparing (2.29b) with (2.17) we see that the eigenvectors $\vec{e}^*(-_j^q)$ and $\vec{e}(_j^q)$ are equal to within a factor of modulus unity:

$$\vec{e}^*(-_j^q) = e^{i\gamma} \vec{e}(_j^q) . \quad (2.30)$$

Since the physical properties do not depend on the choice of the phase factor, we choose $\exp(i\gamma) = 1$ and obtain

$$e^*(\kappa|_j^{-q}) = e(\kappa|_j^q) . \quad (2.31)$$

From (2.14) it follows that

$$\omega_j(q + \tau) = \omega_j(q) , \quad (2.32a)$$

where $\tau = 2\pi m/a$ and $m = 0, \pm 1, \pm 2, \dots$. We show in Appendix A that the atomic displacements are also the same for the modes $(_j^q)$ and $(_j^{q+\tau})$. The displacement

of atom (κ^{ℓ}) in the mode (j^q) is $u(\kappa^{\ell}|j^q)$ and is obtained from (2.7) by replacing $\omega(q)$ by $\omega_j(q)$, $e(\kappa|q)$ by $e(\kappa|j^q)$ and $A(q)$ by $A(j^q)$ and we obtain

$$u(\kappa^{\ell}|j^{q+\tau}) = u(\kappa^{\ell}|j^q) . \quad (2.32b)$$

Thus, a range of $2\pi/a$ for q contains all possible frequencies and all possible patterns of atomic displacements. We want both positive and negative values of q because waves can propagate to the right or to the left; the range of independent values of q is therefore specified by

$$-\pi/a < q \leq \pi/a . \quad (2.33)$$

This range of values of q is referred to as the first *Brillouin zone* of the linear chain, and the points defined by $2\pi m/a$ define the corresponding *reciprocal lattice*. Furthermore, for periodic boundary conditions, the allowed values of q in this zone are determined by (2.1,2,7) which gives $\exp(iqaN) = 1$ or

$$q_m = 2\pi m/Na , \quad (2.34)$$

where m are the integers lying in the interval between $-N/2$ and $N/2$. Thus, if N is even

$$-\frac{1}{2}N < m \leq \frac{1}{2}N . \quad (2.35)$$

If N is odd, the upper limit is to be replaced by $[N/2]$ which is the largest integer smaller than $N/2$. There are exactly N different values of q in the first Brillouin zone and successive values are separated by $2\pi/Na$.

2.1.3 An Illustration: The Linear NaCl-Chain; Transition to the Monoatomic Lattice

As a special example of the diatomic chain discussed in Sects.2.2.1, 2.2.2, we consider the linear NaCl crystal. The lattice parameter is a and the distance between neighbouring Na and Cl atoms is $a/2$. The force constants f and g are equal and we can choose $x(1) = 0$, $x(2) = a/2$. A consequence of the fact that each atom is at a centre of symmetry is, that in the basis of our solution (2.7), both the dynamical matrix $D(q)$ defined by (2.12) and the eigenvector matrix $e(q)$ appearing in (2.17) become real matrices [this would not be the case if in (2.7b) we would write $x(\ell)$ instead of $x(\kappa^{\ell})$].

From (2.14) we obtain

$$\omega_{1,2}^2(q) = \frac{f}{\mu} \left[1 \pm \left(1 - 4 \frac{\mu^2}{m_1 m_2} \sin^2 \frac{aq}{2} \right)^{\frac{1}{2}} \right] . \quad (2.36)$$

For small values of q ($aq \ll 1$), the roots of (2.36) are

$$\omega_1^2(q) \approx \frac{f}{2(m_1 + m_2)} a^2 q^2 \quad (\text{acoustic branch}) \quad (2.37)$$

$$\omega_2^2(q) \approx \frac{2f}{\mu} \quad (\text{optic branch}) . \quad (2.38)$$

For $q = \pi/a$ and $m_1 > m_2$ we find

$$\omega_1^2(\pi/a) = \frac{2f}{m_1} \quad (\text{acoustic branch}) \quad (2.39)$$

$$\omega_2^2(\pi/a) = \frac{2f}{m_2} \quad (\text{optic branch}) . \quad (2.40)$$

The longitudinal-acoustic (LA) and the longitudinal-optic (LO) branches of the dispersion $\omega(q)$ are shown in Fig.2.4. It is important to realize that propagating waves of the form (2.7) do not exist for frequencies between $(2f/m_1)^{1/2}$ and $(2f/m_2)^{1/2}$. This is a characteristic feature of elastic waves in diatomic lattices. There is a *frequency gap* at the zone boundary $q_{\max} = \pm\pi/a$ of the first Brillouin zone. If we look for solutions in the gap with real frequencies ω , then we find from (2.36) that the wave number q will become complex. But a wave of the form $A \exp(iqx)$ with $q = q_1 + iq_2$ is damped in space with a damping factor $\exp(-q_2 x)$. The same is true for frequencies larger than $(2f/\mu)^{1/2}$ [2.1]. Similar results are obtained for the doubly degenerate transverse-acoustic (TA) and transverse-optic (TO) branches with displacements parallel to the y and z -axis in Fig.2.1, that is, perpendicular to the direction of propagation of the wave. However, the frequencies of the transverse vibrations will, in general, be smaller than those of the longitudinal vibrations.

Let us calculate the patterns of displacements of the linear NaCl chain for $q = 0$ and $q = \pi/a$. To do this we calculate the ratio of the amplitudes $m_k^{-1/2} e(k|j)$ for the two atoms 1 and 2. The ratio $e(1|j)/e(2|j)$ follows from (2.16) and (2.12) specialized to the NaCl chain, that is, $f = g$, $x(1) = 0$, $x(2) = a/2$. We obtain

$$r_j(q) = \frac{m_1^{-1/2} e(1|j)}{m_2^{-1/2} e(2|j)} = \frac{2f \cos \frac{aq}{2}}{2f - m_1 \omega_j^2(q)} . \quad (2.41)$$

For the LA branch ($j = 1$), we obtain from (2.37,39,41)

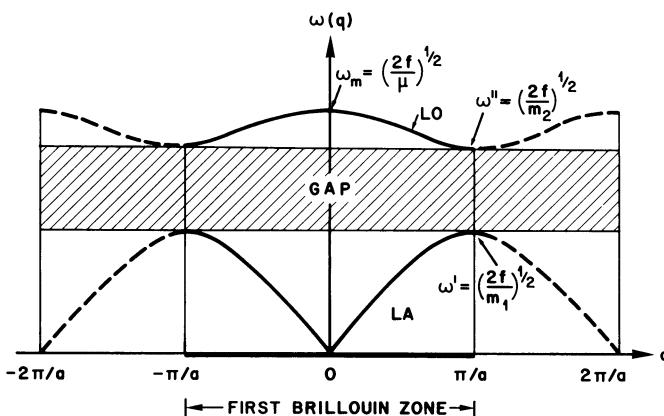


Fig. 2.4. Dispersion of the longitudinal-acoustic (LA) and longitudinal-optic (LO) branches of the diatomic chain with $m_1 > m_2$. The two branches are separated by a gap in which elastic waves cannot propagate

$$r_1(q = 0) = 1 \quad (\text{translation of the whole chain})$$

$$r_1(q = \pi/a) = \infty \quad (\text{amplitude } e(2|_1^q) = 0, \text{ hence only } m_1 \text{ is moving}) .$$

To obtain the latter result, it is necessary to evaluate $r_1(\pi/a + \epsilon)$ for $\epsilon \rightarrow 0$. For the LO branch ($j = 2$), we obtain from (2.38,40,41)

$$r_2(q = 0) = -\frac{m_2}{m_1} \quad (\text{neighbouring atoms are moving in opposite directions})$$

$$r_2(q = \pi/a) = 0 \quad (\text{amplitude } e(1|_2^q) = 0, \text{ hence only } m_2 \text{ is moving}).$$

Similar results apply for the transverse modes. Figure 2.5 shows the LA, LO, TA and TO modes for $q = 0$ and $q = \pi/a$ of the linear NaCl crystal. Substituting (2.36) in (2.41) gives the ratios $r_j(q)$ for all values of q . The qualitative behaviour of these curves for the acoustic and optic branches is shown in Fig. 2.6. From (2.16) and (2.12) we can determine only the ratios $r_j(q)$. If we use, in addition, the relations (2.25,26), we can determine the individual amplitudes $e(\kappa|_j^q)$. For the case of the linear NaCl chain we obtain

$$e(1|_1^q) = \tilde{r}_1(q)w_1(q) , \quad e(1|_2^q) = \tilde{r}_2(q)w_2(q)$$

$$e(2|_1^q) = w_1(q) , \quad e(2|_2^q) = w_2(q) , \quad (2.42)$$

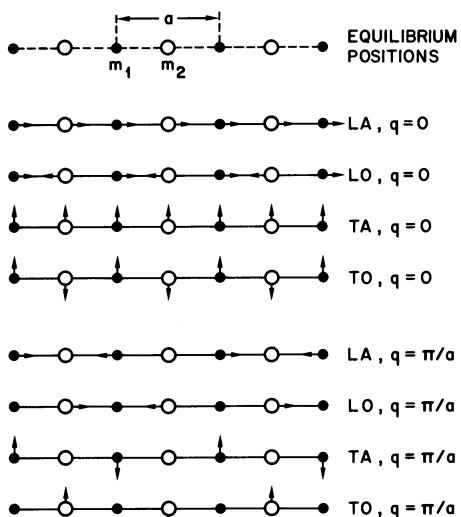


Fig.2.5 ▲

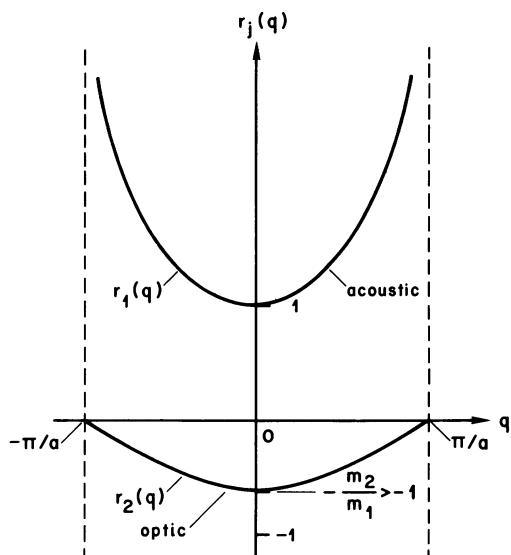


Fig.2.6 ►

Fig.2.5. Patterns of atomic displacements for the longitudinal (LA, LO) and transverse (TA, TO) modes at $q = 0$ and $q = \pi/a$ of the diatomic chain. The arrows indicate the displacements of the atoms with masses $m_1 > m_2$; a is the lattice parameter. Similar patterns of displacements are obtained for elastic waves in alkali halides which propagate in directions of high symmetry (parallel to (111) in NaCl, or parallel to (100) in CsCl); in these cases, entire planes containing only one kind of ion vibrate against each other and the arrows indicate the displacements of these planes

Fig.2.6. Mass weighted amplitude ratios $r_j(q)$ according to (2.41). It is assumed that $m_1 > m_2$. The ratios $r_j(q = 0)$ and $r_j(q = \pi/a)$ correspond to the patterns of displacements illustrated in Fig.2.5

where $\tilde{r}_j(q) = (m_1/m_2)^{\frac{1}{2}} r_j(q)$ and $w_j(q) = [1 + \tilde{r}_j^2(q)]^{-\frac{1}{2}}$. This completely determines the eigenvectors (2.22).

At the end of this section, we discuss the transition from the linear NaCl chain to the monoatomic chain. Such a transition can be achieved by letting $m_1 \rightarrow m_2 = m$. Figure 2.7 shows the dispersion relation similar to Fig.2.5 but with m_1 only slightly larger than m_2 (solid lines). If $m_1 = m_2$, the LO and TO branches join at π/a . In this case, the period is halved and the lattice constant is $d = a/2$. When the lattice period drops from a to $a/2$, the wave number period jumps from $2\pi/a$ to $4\pi/a$. Another change in the dispersion curve is that it must become a single curve since we now have only one degree of freedom in the new unit cell. The single curve is drawn as a dotted line in Fig.2.7, assuming that $m_1, m_2 \rightarrow m = 2\mu$ simultaneously. This

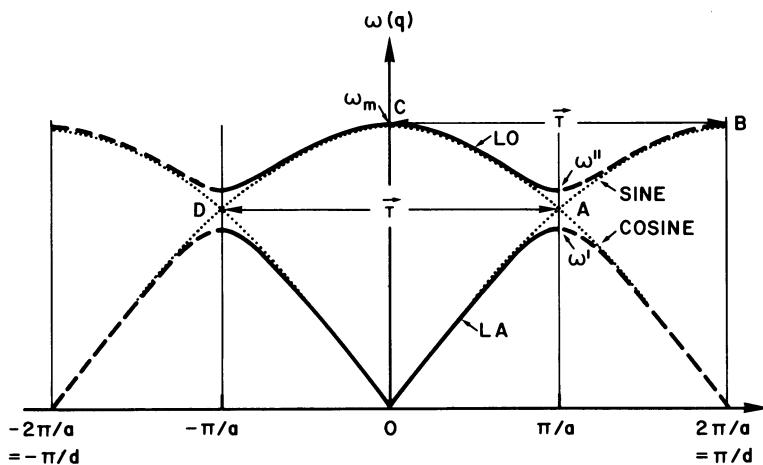


Fig.2.7. Transition from the diatomic to the monoatomic linear chain. Detailed explanations are given in the text

curve is obtained from (2.36) if we take $m_1 = m_2 = m$. The result is

$$\omega^2(q) = \frac{2f}{m} \left(1 \pm \cos \frac{aq}{2}\right) = \begin{cases} \frac{4f}{m} \sin^2 \frac{dq}{2} \\ \frac{4f}{m} \cos^2 \frac{dq}{2} \end{cases}. \quad (2.43)$$

Selecting the sine function we obtain

$$\omega(q) = 2\left(\frac{f}{m}\right)^{\frac{1}{2}} \left| \sin \frac{dq}{2} \right|. \quad (2.44)$$

The cosine curve duplicates the results and in its middle part represents the upper LO curve in Fig.2.7. We note that the optical vibration at $q = 0$ of the diatomic chain becomes an acoustic vibration at $q = \pi/d$ of the monoatomic chain. The upper part AB of the sine curve in Fig.2.7 can be obtained by folding out the LO branch AC, or equivalently, by translation of the LO branch CD through $2\pi/a$, that is, by a reciprocal lattice vector $\vec{T} = \vec{BA}$. This is called an *Umplapp process*. The dispersion relation (2.43) can of course be obtained if we start directly with the Hamiltonian of the monoatomic chain which follows easily from (2.3) and then solving the resulting equations of motion by assuming a solution of the form

$$u(\varrho) = (Nm)^{-\frac{1}{2}} |A(q)| \cos[qd\varrho - \omega(q)t + \alpha(q)],$$

where, as in (2.7a), the amplitude $|A(q)|$ and the phase $\alpha(q)$ are determined by the initial conditions.

2.1.4 Normal Coordinates

From (2.7b) the displacement of atom (κ^{ℓ}) in the mode (qj) is given by

$$u(\kappa^{\ell}|j^q) = \frac{1}{2} (Nm_{\kappa})^{-\frac{1}{2}} [A(j^q)e(\kappa|j^q) \exp\{i[qx(\kappa^{\ell}) - \omega_j(q)t]\} + c.c.] . \quad (2.45)$$

Equation (2.45) represents a *special solution* to the equation of motion (2.6). According to (2.33,35), there are N independent values of q lying in the first Brillouin zone $-\pi/a < q \leq \pi/a$. If $q > 0$, $A(j^q)$ is the amplitude of a wave travelling to the right while $A(-j^q)$ is a wave travelling to the left. Since the two waves are independent, there are no necessary conditions between $A(j^q)$ and $A(-j^q)$. The *general solution* will therefore be a superposition of solutions of the type (2.45), where the summation extends over all modes (qj) :

$$\begin{aligned} u(\kappa^{\ell}) &= \frac{1}{2} (Nm_{\kappa})^{-\frac{1}{2}} \sum_{qj} [A(j^q)e(\kappa|j^q) \exp\{i[qx(\kappa^{\ell}) - \omega_j(q)t]\} + c.c.] \\ &= \frac{1}{2} (Nm_{\kappa})^{-\frac{1}{2}} \sum_{j, q \geq 0} [A(j^q)e(\kappa|j^q) \exp\{i[qx(\kappa^{\ell}) - \omega_j(q)t]\} + c.c.] \\ &\quad + \frac{1}{2} (Nm_{\kappa})^{-\frac{1}{2}} \sum_{j, q > 0} [A(-j^q)e(\kappa|-j^q) \exp\{i[-qx(\kappa^{\ell}) - \omega_j(-q)t]\} + c.c.] . \end{aligned} \quad (2.46)$$

More formally, the general solution can be expressed in terms of N *complex normal coordinates* $Q(j^q)$ by the following transformation:

$$\begin{aligned} u(\kappa^{\ell}) &= (Nm_{\kappa})^{-\frac{1}{2}} \sum_{qj} e(\kappa|j^q) \exp[iqx(\kappa^{\ell})] Q(j^q) \\ &= (Nm_{\kappa})^{-\frac{1}{2}} \sum_{j, q \geq 0} e(\kappa|j^q) \exp[iqx(\kappa^{\ell})] Q(j^q) \\ &\quad + (Nm_{\kappa})^{-\frac{1}{2}} \sum_{j, q > 0} e(\kappa|-j^q) \exp[-iqx(\kappa^{\ell})] Q(-j^q) . \end{aligned} \quad (2.47)$$

Since $u(\kappa^{\ell})$ is real [$u^*(\kappa^{\ell}) = u(\kappa^{\ell})$], we obtain from (2.47)

$$Q(-j^q) = Q^*(j^q) . \quad (2.48)$$

Comparison of (2.46,47) and using (2.28,31) yields

$$Q_j^q = \frac{1}{2} [A_j^q e^{-i\omega_j(q)t} + A_j^{*-q} e^{i\omega_j(q)t}] . \quad (2.49)$$

The amplitudes A_j^q and A_j^{*-q} are associated with a wave travelling to the right while A_j^{-q} and A_j^{*q} are associated with a wave travelling to the left. Note that A_j^q and A_j^{-q} are independent because they are given by the initial conditions, but that Q_j^q and Q_j^{-q} are not independent because of (2.48). Equation (2.49) shows that it is not correct to associate Q_j^q with a wave travelling in the positive direction only, because Q_j^q involves both A_j^q and A_j^{*-q} .

We can solve (2.47) for Q_j^q by multiplying both sides with $(Nm_k)^{\frac{1}{2}} e^{*(k|j)} \exp[-iq'x(\frac{k}{a})]$ and summing over k and λ which gives

$$\begin{aligned} \sum_{qj} Q_j^q \sum_k e^{*(k|j)} e^{(k|j)} e^{i(q-q')x(k)} \sum_\lambda e^{i(q-q')\lambda a} \\ = \sum_{k\lambda} (Nm_k)^{\frac{1}{2}} e^{*(k|j)} \exp[-iq'x(\frac{k}{a})] u(\frac{k}{a}) . \end{aligned} \quad (2.50)$$

In Appendix B we prove that

$$\sum_\lambda e^{i(q-q')\lambda a} = N\Delta(q - q') , \quad (2.51)$$

where

$$\begin{aligned} \Delta(q - q') = 1 & \quad \text{for } q = q' \pm \frac{2\pi n}{a} \\ \Delta(q - q') = 0 & \quad \text{otherwise} . \end{aligned} \quad (2.52)$$

Application of (2.51,52) and (2.25) to (2.50) immediately gives

$$Q_j^q = N^{-\frac{1}{2}} \sum_{k\lambda} m_k^{\frac{1}{2}} e^{*(k|j)} \exp[-iqx(\frac{k}{a})] u(\frac{k}{a}) . \quad (2.53)$$

Equation (2.53) shows that the normal coordinates Q_j^q are *collective coordinates* because the sum extends over all the local atomic displacement coordinates $u(\frac{k}{a})$.

Substituting $u(\frac{k}{a})$ from (2.47) into the Hamiltonian H of (2.3), we can express H in terms of the normal coordinates Q_j^q . A certain amount of algebra is required to obtain the result which is derived in Appendix C. One obtains

$$H = T + \Phi = \frac{1}{2} \sum_{qj} [|\dot{Q}_j^q|^2 + \omega_j^2(q)|Q_j^q|^2] \quad (2.54)$$

with $\omega_j^2(q)$ given by (2.14). The main achievement of introducing the normal coordinates is that the structure of the Hamiltonian (2.54) is much simpler than the Hamiltonian (2.3). However, it should be emphasized here that the Hamilton function (2.54) is still not yet completely diagonal with respect to q . In fact, using (2.48) we note that there are still mixed terms of the form $Q(j)Q(-j)$ and $\dot{Q}(j)\dot{Q}(-j)$.

From the Lagrangian $L = T - \phi$, the momentum conjugate to $Q(j)$ is

$$P(j) = \frac{\partial L}{\partial \dot{Q}^*(j)} = \frac{\partial T}{\partial \dot{Q}^*(j)} = \dot{Q}(j) \quad (2.55)$$

and using (2.53) and (2.4) we obtain

$$P(j) = N^{-1/2} \sum_{\ell \in K} m_{\ell}^{-1/2} e^{*(\kappa|j)} \exp[-iqx(\ell)] p(\ell) \quad (2.56)$$

Replacing q by $-q$ in this equation and using (2.31) we obtain

$$P(-j) = P^*(j) \quad (2.57)$$

which is the analogous equation to (2.48). Using (2.55), the Hamiltonian (2.54) can also be written in the form

$$H = \frac{1}{2} \sum_{qj} [|P(j)|^2 + \omega_j^2(q) |Q(j)|^2] \quad . \quad (2.58)$$

From Hamiltonians equations of motion

$$\dot{Q}(j) = \frac{\partial H}{\partial P^*(j)} \quad (2.59)$$

$$\dot{P}(j) = - \frac{\partial H}{\partial Q^*(j)} \quad , \quad (2.60)$$

it is found from (2.58) that the equation of motion of the complex normal coordinate $Q(j)$ is given by the uncoupled harmonic oscillator equation

$$\ddot{Q}(j) + \omega_j^2(q) Q(j) = 0 \quad . \quad (2.61)$$

By definition (2.53) the normal coordinates $Q(j)$ are complex quantities. For many applications and, in particular, for effecting the transition to quantum mechanics, it is more convenient to re-express the complex normal coordinates in terms of *real* normal coordinates [2.2,6]. The most obvious way of expressing $Q(j)$ in terms of real normal coordinates is as follows:

$$\begin{aligned} Q_j^q &= \frac{1}{\sqrt{2}} [\alpha_1(j)^q + i\alpha_2(j)^q] \\ Q_j^{*q} &= \frac{1}{\sqrt{2}} [\alpha_1(j)^q - i\alpha_2(j)^q] \quad . \end{aligned} \quad (2.62)$$

From (2.62) it immediately follows that $\alpha_1(-j)^q = \alpha_1(j)^q$ and $\alpha_2(-j)^q = -\alpha_2(j)^q$, so that only half of the real normal coordinates $\{\alpha_v(j)^q\}$ are independent and we have as many independent normal coordinates as there are degrees of freedom ($2N$ for the longitudinal modes of the diatomic chain with N unit cells). The independent normal coordinates $\{\alpha_v(j)^q\}$ are thus obtained by restricting q to positive values of the first Brillouin zone. Substitution of (2.62) in (2.54) gives

$$\begin{aligned} H &= \frac{1}{2} \sum_{q>0} \sum_j [\dot{Q}(-j)^q \dot{Q}(j)^q + \omega_j^2(q) Q(-j)^q Q(j)^q] \\ &\quad + \frac{1}{2} \sum_{q>0} \sum_j [\dot{Q}(j)^q \dot{Q}(-j)^q + \omega_j^2(q) Q(j)^q Q(-j)^q] \\ &= \frac{1}{2} \sum_{q>0} \sum_{v=1,2} [\dot{\alpha}_v(j)^q + \omega_j^2(q) \alpha_v^2(j)^q] \quad . \end{aligned} \quad (2.63)$$

The form (2.63) confirms that $\{\alpha_v(j)^q\}$'s are normal coordinates of the system. In addition we notice that in contrast to (2.54) and (2.58), the Hamiltonian is now completely diagonal with respect to q . By substitution of (2.62) in (2.47) and using (2.10) in the form $e(\kappa|j)^q = |e(\kappa|j)| \exp[i\varphi(\kappa|j)^q]$, it can be easily shown that the coordinates $\alpha_1(j)^q$ and $\alpha_2(j)^q$ are the amplitudes of two standing waves which are shifted with respect to each other by a quarter wave. This means that if $u(\kappa)$ is expressed in terms of the $\{\alpha_v(j)^q\}$ using (2.47), the coefficient of $\alpha_1(j)^q$ is proportional to $\cos[qx(\kappa) + \varphi(\kappa|j)^q]$ while the coefficient of $\alpha_2(j)^q$ is proportional to $\sin[qx(\kappa) + \varphi(\kappa|j)^q]$. These coordinates are also referred to as real normal coordinates of the first kind [2.6].

It is also possible to define real normal coordinates $n(j)^q$ which describe running waves. In contrast to the real normal coordinates $\alpha_v(j)^q$, the coordinates $n(j)^q$ are not just linear combinations of $Q(j)^q$ and $Q^*(j)^q$ but also of the momenta $P(j)^q$ and $P^*(j)^q$. They are coordinates which can be obtained by a canonical transformation, but we shall introduce them here in an elementary way as follows [2.6]:

$$Q_j(q) = \frac{i}{2} [\dot{n}_j(-q) - n_j(q)] + \frac{1}{2\omega_j(q)} [\dot{\eta}_j(-q) + \dot{\eta}_j(q)] . \quad (2.64)$$

First we notice that if we replace q by $-q$ in (2.64) we obtain $Q_j^*(q)$, that is, the reality condition (2.48) is satisfied. Assuming that $n_j(q)$ satisfies the uncoupled harmonic oscillator equation (an assumption which will be verified below), we have that

$$\ddot{\eta}_j(q) + \omega_j^2(q) \eta_j(q) = 0 . \quad (2.65)$$

Forming $P_j(q) = \dot{Q}_j(q)$ from (2.64) and using (2.65) we obtain

$$P_j(q) = \frac{i}{2} [\dot{n}_j(-q) - \dot{n}_j(q)] - \frac{1}{2} \omega_j(q) [n_j(-q) + n_j(q)] . \quad (2.66)$$

From (2.64,66) we can solve for $n_j(q)$ and $\zeta_j(q) = \dot{\eta}_j(q)$. Forming $Q_j^*(q) = Q_j(-q)$ and $P_j^*(q) = P_j(-q)$ and observing that $\omega_j(-q) = \omega_j(q)$, one obtains

$$n_j(q) = \frac{i}{2} [Q_j(q) - Q_j^*(q)] - \frac{1}{2\omega_j(q)} [P_j(q) + P_j^*(q)] \quad (2.67)$$

$$\zeta_j(q) = \frac{i}{2} [P_j(q) - P_j^*(q)] + \frac{1}{2} \omega_j(q) [Q_j(q) + Q_j^*(q)] . \quad (2.68)$$

In deriving (2.68) from (2.67) we have used $\dot{Q}_j(q) = P_j(q)$ and (2.61). According to (2.67,68), the coordinates $n_j(q)$ and the conjugate momenta $\zeta_j(q)$ are defined for all q -values in the first Brillouin zone $-\pi/a < q \leq \pi/a$. It can be shown [2.6] that these real coordinates $n_j(q)$ represent *running waves*. They are also referred to as *normal coordinates of the second kind*.

Substituting (2.64,66) in (2.58), one obtains

$$H = \frac{1}{2} \sum_{q,j} [\dot{n}_j^2(q) + \omega_j^2(q) n_j^2(q)] . \quad (2.69)$$

The form of this expression shows that the $n_j(q)$ are in fact normal coordinates of the system, thereby also justifying the assumption (2.65). As for (2.63), the Hamiltonian function (2.69) is now completely diagonal with respect to q .

At this point the following remarks should be made:

- a) By introducing the coordinates $Q_j(q)$, $\alpha_v(q)$, and $\eta(q)$, we have been able to decompose the vibrations into a system of $2N$ independent harmonic oscillators corresponding to the $2N$ degrees of freedom for the longitudinal vibrations of the diatomic chain with N unit cells. $Q_j(q)$, $\alpha_v(q)$ and $\eta(q)$ all satisfy

fy uncoupled harmonic oscillator equations such as (2.61,65). To each normal coordinate $Q_j(q)$, $\alpha_v(j)$ or $\eta(j)$ belongs an eigenvalue

$$\lambda_j(q) = \omega_j^2(q) \quad (2.70)$$

defined by (2.14) and a pattern of atomic displacements such as those shown in Fig.2.5.

b) Since the wave functions of the harmonic oscillator depend on *real* coordinates such as $\alpha_v(j)$ or $\eta(j)$, the Schrödinger equations corresponding to the Hamilton functions (2.63,69) can be obtained immediately. The quantization of the system is thereby reduced to the standard wave mechanics of simple harmonic oscillators.

c) From (2.49,55) we obtain

$$Q_j(q) = \frac{1}{2} \left[A^*(-j)e^{i\omega_j(q)t} + A(j)e^{-i\omega_j(q)t} \right] \quad (2.71)$$

$$P_j(q) = \frac{1}{2} i\omega_j(q) \left[A^*(-j)e^{i\omega_j(q)t} - A(j)e^{-i\omega_j(q)t} \right] . \quad (2.72)$$

These equations will be important for the introduction of creation and annihilation operators appearing in the occupation number representation of quantum mechanics (Sects.2.2.3,4).

d) Substituting (2.71,72) in (2.58), it is easily shown that the total mean energy of the system is

$$\bar{E} = \frac{1}{2} \sum_{qj} \omega_j^2(q) |A(j)|^2 = \sum_{qj} \bar{E}_j(q) , \quad (2.73)$$

where $j = 1,2$ if we confine ourselves to the longitudinal vibrations and q assumes the N -values in the first Brillouin zone. Thus, (2.73) is the energy of $2N$ independent harmonic oscillators. For a system obeying the laws of classical physics and in thermal equilibrium with a heat bath at temperature T , we have, according to the principle of equipartition [2.7],

$$\bar{E}_j(q) = \frac{1}{2} \omega_j^2(q) |A(j)|^2 = k_B T \quad (2.74)$$

and

$$\bar{E} = 2Nk_B T . \quad (2.75)$$

Here, k_B is the Boltzmann constant. The classical specific heat due to the longitudinal vibrations of the diatomic chain with N unit cells is therefore

$$c_V = \frac{d\bar{E}}{dT} = 2Nk_B , \quad (2.76)$$

independent of temperature; this is contrary to what is found experimentally. The difficulty can be solved by quantization of the lattice vibrations which gives the result that $c_V(T)$ tends to zero as T approaches zero in agreement with experiment (Sect.2.2.4).

2.2 Quantum Mechanics

Before developing the occupation number representation outlined in Sects. 2.2.3,4, we begin with the more familiar Schrödinger equation formulation. In Sect.2.2.2 we shall demonstrate that each term of the Hamilton functions (2.63) or (2.69) can be quantized as a simple harmonic oscillator. We therefore start with the wave mechanics of a simple oscillator.

2.2.1 The Schrödinger Equation of the Simple Harmonic Oscillator

In this section we summarize the wave mechanics of the harmonic oscillator. Excellent treatments are given in [2.8,9].

We consider a harmonic oscillator with mass m , displacement coordinate u and momentum $p = m\dot{u}$. The classical Hamilton function is

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 u^2 . \quad (2.77)$$

The transition to quantum mechanics is achieved by replacing the momentum p by the operator

$$p = -i\hbar \frac{\partial}{\partial u} . \quad (2.78)$$

It is more convenient to introduce the new coordinate $\eta = m^{1/2}u$ and the corresponding momentum $\zeta = \dot{\eta} = m^{-1/2}p$ in terms of which H assumes the form

$$H = \frac{1}{2} (\zeta^2 + \omega^2 \eta^2) \quad (2.79)$$

and from (2.78) the momentum operator corresponding to ζ is

$$\zeta = -i\hbar \frac{\partial}{\partial \eta} . \quad (2.80)$$

Introducing (2.80) in (2.79) we obtain the Hamilton operator

$$H = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial \eta^2} + \frac{1}{2} \omega^2 \eta^2 \quad (2.81)$$

and the Schrödinger equation is

$$H\psi_n(\eta) = E_n \psi_n(\eta) \quad (2.82)$$

or

$$\left(-\frac{\hbar^2}{2} \frac{\partial^2}{\partial \eta^2} + \frac{1}{2} \omega^2 \eta^2 \right) \psi_n(\eta) = E_n \psi_n(\eta) , \quad (2.83)$$

where E_n is the eigenvalue and ψ_n the eigenfunction of the oscillator in the state with quantum number n . It is well known that the eigenvalues are given by [2.8,9]

$$E_n = \hbar\omega(n + \frac{1}{2}) \quad (2.84)$$

and the eigenfunctions are

$$\psi_n(\eta) = N_n e^{-\frac{1}{2}\gamma n^2} H_n(\gamma^{\frac{1}{2}}\eta) , \quad (2.85)$$

where

$$\gamma = \frac{\omega}{\hbar} \quad (2.86)$$

and N_n is a normalizing constant given by

$$N_n = (\frac{\gamma}{\pi})^{\frac{1}{4}} (2^n n!)^{-\frac{1}{2}} . \quad (2.87)$$

H_n is the n^{th} Hermite polynomial defined by

$$H_n(z) = (-1)^n e^{z^2} \frac{d}{dz^n} e^{-z^2} \quad (2.88)$$

which satisfies the following relations:

$$\frac{\partial}{\partial z} H_n(z) = 2n H_{n-1}(z) \quad (2.89)$$

$$2z H_n(z) = 2n H_{n-1}(z) + H_{n+1}(z) . \quad (2.90)$$

From (2.85-88) it follows that the wave function of the *ground state* ($n = 0$) is given by

$$\psi_0(\eta) = (\frac{\gamma}{\pi})^{\frac{1}{4}} e^{-\frac{1}{2}\gamma\eta^2}$$

and the wave function of the *first excited state* ($n = 1$) is

$$\psi_1(\eta) = \sqrt{2} \left(\frac{\gamma}{\pi}\right)^{1/4} \gamma^{1/2} e^{-\frac{1}{2}\gamma\eta^2} \eta .$$

These functions are shown in Fig.2.8a. The probability density of finding the particle between η and $\eta + d\eta$ is given by $|\psi_n(\eta)|^2$. For the ground state this is

$$|\psi_0(\eta)|^2 = \left(\frac{\gamma}{\pi}\right)^{1/2} e^{-\gamma\eta^2} .$$

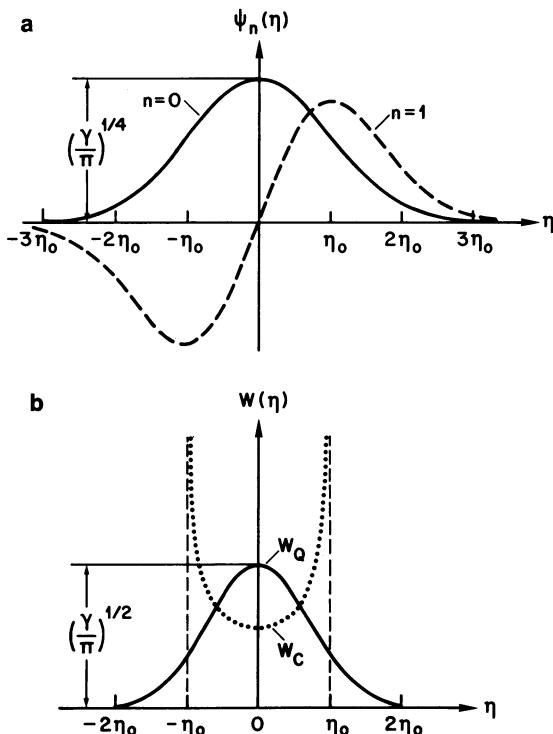


Fig.2.8. a) Wave functions $\psi_0(\eta)$ and $\psi_1(\eta)$ for the ground state ($n=0$) and the first excited state ($n=1$) of the harmonic oscillator ($\eta_0=\gamma^{-1/2}=(\omega/\hbar)^{-1/2}$). b) Quantum mechanical probability density $w_0(\eta) = |\psi_0(\eta)|^2$ (solid line) and classical probability density $w_c(\eta) = (\pi/\eta_0)^{-1} \times (1 - \eta^2/\eta_0^2)^{-1/2}$ (dotted line) for an oscillator with the same total energy

Figure 2.8b shows $|\psi_0(\eta)|^2$ together with the classical probability density for an oscillator with the same total energy (Problem 2.3.3). It is seen from this figure that the quantum mechanical result does not agree at all with the classical result. Classically, the particle is most likely to be found at the ends of its motion at $\eta_m = \gamma^{-1/2}$, whereas $|\psi_0(\eta)|^2$ has its maximum at $\eta = 0$ and shows a rapidly decreasing but nonvanishing probability of

finding the particle outside the region allowed classically. For large quantum numbers n (at high temperatures), however, it can be shown that the average value of $|\psi_n(n)|^2$ closely approximates the classical probability density.

The eigenfunctions (2.85) are orthogonal, that is,

$$\int_{-\infty}^{+\infty} \psi_m^*(n) \psi_n(n) dn = \langle m | n \rangle = \delta_{m,n} . \quad (2.91)$$

Let us calculate the matrix elements of η and of $\zeta = -i\hbar\partial/\partial\eta$:

$$\langle m | \eta | n \rangle = \int_{-\infty}^{+\infty} \psi_m^*(n) \eta \psi_n(n) dn \quad (2.92)$$

$$\langle m | \zeta | n \rangle = -i\hbar \int_{-\infty}^{+\infty} \psi_m^*(n) \frac{\partial}{\partial\eta} \psi_n(n) dn . \quad (2.93)$$

From (2.87) it follows that

$$N_n = 2^{\frac{1}{2}}(n+1)^{\frac{1}{2}} N_{n-1} = 2^{-\frac{1}{2}} n^{-\frac{1}{2}} N_{n-1} . \quad (2.94)$$

Using (2.89, 90, 94), we find for the functions $\eta\psi_n(n) = \eta|n\rangle$ and $\zeta\psi_n(n) = \zeta|n\rangle$ the following results:

$$\eta|n\rangle = \left(\frac{\hbar}{2\omega}\right)^{\frac{1}{2}} [(n+1)^{\frac{1}{2}}|n+1\rangle + n^{\frac{1}{2}}|n-1\rangle] \quad (2.95)$$

$$\zeta|n\rangle = -i\left(\frac{\hbar\omega}{2}\right)^{\frac{1}{2}} [(n+1)^{\frac{1}{2}}|n+1\rangle - n^{\frac{1}{2}}|n-1\rangle] . \quad (2.96)$$

From (2.95, 96) and (2.91) we find

$$\langle m | \eta | n \rangle = \left(\frac{\hbar}{2\omega}\right)^{\frac{1}{2}} [(n+1)^{\frac{1}{2}} \delta_{m,n+1} + n^{\frac{1}{2}} \delta_{m,n-1}] \quad (2.97)$$

$$\langle m | \zeta | n \rangle = i\left(\frac{\hbar\omega}{2}\right)^{\frac{1}{2}} [(n+1)^{\frac{1}{2}} \delta_{m,n+1} - n^{\frac{1}{2}} \delta_{m,n-1}] . \quad (2.98)$$

2.2.2 The Schrödinger Equation of the Vibrating Chain

In Sect. 2.1.4 we have shown that in terms of the real normal coordinates $\alpha_v(q_j)$ or $\eta_j(q)$, the Hamiltonian functions assume the simple and completely diagonalized forms of (2.63) and (2.69), respectively. In terms of the coordinates $\eta_j(q)$ and their conjugate momenta $\zeta_j(q)$ we have obtained

$$H = \frac{1}{2} \sum_{qj} \left[\zeta_j^2(q) + \omega_j^2(q) n_j^2(q) \right] . \quad (2.99)$$

Now, each term in (2.99) represents a simple harmonic oscillator which is described by the real variable $n_j(q)$ and can therefore be directly compared with (2.79). For this reason and because the wave functions depend on real coordinates, each oscillator of (2.99) can be quantized by exactly the same procedure as outlined in Sect.2.2.1. Of course, the same is true for the Hamilton function (2.63) in terms of the real normal coordinates $\alpha_j(q)$, but in the following we proceed with (2.99). In Appendix D, it is shown that from the momentum operator

$$p_k^{\ell} = -i\hbar \frac{\partial}{\partial u_k^{\ell}} ,$$

it follows that the momentum operator corresponding to $\zeta_j(q)$ is given by

$$\zeta_j(q) = -i\hbar \frac{\partial}{\partial n_j(q)} . \quad (2.100)$$

Therefore, the Schrödinger equation of the oscillator $s = (qi)$ is completely analogous to (2.83), that is,

$$\left(-\frac{\hbar^2}{2} \frac{\partial^2}{\partial n_s^2} + \frac{1}{2} \omega_s^2 n_s^2 \right) \psi_{n_s}(n_s) = E_{n_s} \psi_{n_s}(n_s) . \quad (2.101)$$

From the above it is clear that all results developed in Sect.2.2.1 also apply to the linear chain. Of course, now the index $s = (qj)$, must be added everywhere, that is, it is to be understood that $n = n_s = n_j(q)$, $\omega = \omega_s = \omega_j(q)$, $\gamma = \gamma_s = \gamma_j(q)$, $n = n_s = n_j(q)$ in the relations (2.84-98) if they are applied to the diatomic linear chain. As an example, the energy of the oscillator $s = (qj)$ in the state with quantum number n_s is, according to (2.84),

$$E_{n_s} = \hbar \omega_s (n_s + \frac{1}{2}) \quad (2.102)$$

and according to (2.85), the corresponding wave function is given by

$$\psi_{n_s}(n_s) = N_{n_s} e^{-\frac{1}{2}\gamma_s n_s^2} H_{n_s}(\gamma_s n_s) . \quad (2.103)$$

Since the oscillators s are independent, the total wave function ψ of the vibrating system is the product of "single particle" wave functions, that is,

$$\Psi = \prod_s \Psi_{n_s}(q_s) \quad (2.104)$$

and we shall use the notation

$$\begin{aligned} \Psi &= |n_{s_1}, n_{s_2} \dots n_{s_m} \dots n_{s_{2N}}\rangle \\ &= |n_1, n_2, \dots n_m \dots n_{2N}\rangle \quad . \end{aligned} \quad (2.105)$$

For the longitudinal vibrations of the diatomic chain with N unit cells, s_1 stands for $(q_1, j = 1)$ and s_{2N} for $(q_N, j = 2)$. For the "single particle" wave functions we use the corresponding notation

$$\Psi_{n_s} = |n_s\rangle \quad . \quad (2.106)$$

The normalization condition for Ψ is obtained from (2.91,104):

$$\langle n_1, n_2 \dots n_s \dots | m_1, m_2 \dots m_s \dots \rangle = \delta_{n_1 m_1} \delta_{n_2 m_2} \dots \delta_{n_s m_s} \dots \quad . \quad (2.107)$$

The Schrödinger equation of the vibrating chain is

$$H\Psi = E\Psi \quad , \quad (2.108)$$

where Ψ is given by (2.104) and

$$H = \sum_s H_s = \sum_s \left\{ -\frac{\hbar^2}{2} \frac{\partial^2}{\partial q_s^2} + \frac{1}{2} \omega_s^2 n_s^2 \right\} \quad . \quad (2.109)$$

From (2.104,108,109), it follows that the total energy E is the sum of the "single particle" energies E_{n_s} , that is,

$$\begin{aligned} E &= \sum_s E_{n_s} = \sum_{qj} E_{n_j}(q) \\ &= \sum_{qj} \hbar \omega_j(q) \left[n_j(q) + \frac{1}{2} \right] \quad . \end{aligned} \quad (2.110)$$

We have performed the quantization on the basis of the running waves $n_j(q)$ which have the advantage that they are defined for all values in the first Brillouin zone but have the disadvantage that by definition (2.67), they depend on both the coordinates Q and the momenta P . The consequences are that the oscillators can be specified by q and j alone but that the wave functions $\Psi[n_j(q)]$ depend not only on the configurational coordinates Q but also on the momenta P , which is not a very familiar situation. We could have performed the quantization just as well on the basis of the standing waves $\alpha_v(j)$ which have the advantage that they depend only on the coordinates Q (2.62), but

the disadvantage that they are defined only for positive values of q in the Brillouin zone. In this case, $\psi[\alpha_v(q_j)]$ depends only on the configurational coordinates Q as we are accustomed, but we now need three indices to specify the oscillators, namely, q , j , and $v = 1, 2$.

2.2.3 Creation and Annihilation Operators

The quantum mechanical description of lattice vibrations and other elementary excitations becomes particularly transparent if one introduces creation and annihilation operators. This procedure is also known as "second quantization" and is an alternative description to the one given in Sect. 2.2.2. We give here a short résumé of the method. More detailed treatments are found in [2.10,11].

To begin with, we calculate the quantum mechanical commutators $[Q^*(q_j), P(q'_{j'})] = Q^*(q_j)P(q'_{j'}) - P(q'_{j'})Q^*(q_j)$, etc., of the operators $Q^*(q_j)$ and $P(q'_{j'})$. Using the expression derived from (2.53) for $Q^*(q_j)$, the expression obtained from (2.56) for $P(q'_{j'})$ and the well-known commutators (Appendix D)

$$\begin{aligned} [u(\ell_k), p(\ell'_{k'})] &= i\hbar\delta_{kk'}\delta_{\ell\ell'}, \\ [u(\ell_k), u(\ell'_{k'})] &= [p(\ell_k), p(\ell'_{k'})] = 0 \quad , \end{aligned} \quad (2.111)$$

we obtain, with the help of (2.25,51), (Appendix D)

$$[Q^*(q_j), P(q'_{j'})] = i\hbar\Delta(q - q')\delta_{jj'} \quad (2.112a)$$

$$[Q(q_j), P^*(q'_{j'})] = i\hbar\Delta(q - q')\delta_{jj'} \quad (2.112b)$$

$$[Q^*(q_j), Q(q'_{j'})] = [P^*(q_j), P(q'_{j'})] = 0 \quad . \quad (2.112c)$$

We now define operators $a(j)$ and $a^+(j)$ by means of the relations

$$Q(q_j) = \left(\frac{\hbar}{2\omega_j(q)} \right)^{\frac{1}{2}} [a^+(-q_j) + a(q_j)] \quad (2.113)$$

$$P(q_j) = i \left(\frac{\hbar\omega_j(q)}{2} \right)^{\frac{1}{2}} [a^+(-q_j) - a(q_j)] \quad . \quad (2.114)$$

The analogous equations in classical mechanics are (2.71,72). Note that we have introduced $a^+(-q_j)$ and not $a^+(q_j)$, in complete analogy with the classical case. In fact, the comparison of the above equations with (2.71,72) shows that $A^*(-q_j) \exp[i\omega_j(q)t]$ corresponds to $a^+(-q_j)$ while $A(q_j) \exp[-i\omega_j(q)t]$ cor-

responds to $a_j^-(q)$. Remembering the discussion in Sect. 2.1.4, this means that $a_j^-(q)$ is associated with a wave travelling to the right while $a_j^+(\neg q)$ is associated with a wave travelling to the left.

The inverse transformation of (2.113,114) gives

$$a_j(q) = \left(\frac{\omega_j(q)}{2\hbar}\right)^{\frac{1}{2}} Q_j(q) + i \left(\frac{1}{2\hbar\omega_j(q)}\right)^{\frac{1}{2}} P_j(q) \quad (2.115)$$

$$a_j^+(\neg q) = \left(\frac{\omega_j(q)}{2\hbar}\right)^{\frac{1}{2}} Q_j(q) - i \left(\frac{1}{2\hbar\omega_j(q)}\right)^{\frac{1}{2}} P_j(q) . \quad (2.116)$$

We are interested in commutators of the form $[a_j^-(q), a_j^+(\neg q)]$, etc. Replacing $(\neg q)$ by (q') in (2.116) and using $\omega_j(-q') = \omega_j(q')$ as well as (2.48,57), we obtain

$$a_j^+(\neg q') = \left(\frac{\omega_j(q')}{2\hbar}\right)^{\frac{1}{2}} Q_j^*(q') - i \left(\frac{1}{2\hbar\omega_j(q')}\right)^{\frac{1}{2}} P_j^*(q') .$$

Substituting $a_j(q)$ and $a_j^+(\neg q')$ in $[a_j(q), a_j^+(\neg q')]$ and using (2.112), we find

$$\begin{aligned} [a_j(q), a_j^+(\neg q')] &= \Delta(q - q') \delta_{jj}, \\ [a_j(q), a_j(q')] &= [a_j^+(q), a_j^+(\neg q')] = 0 . \end{aligned} \quad (2.117)$$

From (2.58), the Hamilton operator in terms of the operators $Q_j(q)$ and $P_j(q)$ is given by

$$H = \frac{1}{2} \sum_{qj} [P_j^*(q)P_j(q) + \omega_j^2(q)Q_j^*(q)Q_j(q)] . \quad (2.118)$$

We express H in terms of the operators $a_j^+(\neg q)$ and $a_j^-(q)$. Substitution of (2.113,114) in (2.118) and using (2.117) gives the simple result

$$H = \sum_{qj} H_j(q) = \sum_{qj} \hbar\omega_j(q)[a_j^+(\neg q)a_j^-(q) + \frac{1}{2}] . \quad (2.119)$$

Acting with H given by (2.119) on the total wave function $\psi = | \dots n_s \dots \rangle$ and again using the condensed notation $a_s^+ = a_j^+(\neg q)$, $\omega_s = \omega_j(q)$, etc., we obtain

$$\begin{aligned} H| \dots n_s \dots \rangle &= \sum_s \hbar\omega_s (a_s^+ a_s^- + \frac{1}{2}) | n_{s_1} \dots n_s \dots \rangle \\ &= E| \dots n_s \dots \rangle = \sum_s \hbar\omega_s (n_s + \frac{1}{2}) | n_{s_1} \dots n_s \dots \rangle , \end{aligned}$$

where we have used (2.110) for the total energy E . From this it follows that

$$a_s^+ a_s |n_{s_1} \dots n_s \dots> = n_s |n_{s_1} \dots n_s \dots> \quad (2.120)$$

$$a_s a_s^+ |n_{s_1} \dots n_s \dots> = (n_s + 1) |n_{s_1} \dots n_s \dots> . \quad (2.121)$$

Thus, $|n_{s_1} \dots n_s \dots>$ are eigenfunctions of the operators $a_s^+ a_s$ and $a_s a_s^+$ belonging to the eigenvalues n_s and $n_s + 1$, respectively. Since the eigenvalue of $a_s^+ a_s$ is just n_s , the operator $a_s^+ a_s$ is also referred to as the *number operator*.

In Appendix E, we prove the following important relations:

$$a_s^+ | \dots n_s \dots > = (n_s + 1)^{\frac{1}{2}} | \dots n_s + 1 \dots > \quad (2.122)$$

$$a_s | \dots n_s \dots > = n_s^{\frac{1}{2}} | \dots n_s - 1 \dots > . \quad (2.123)$$

According to (2.122,123), the operators a_s^+ and a_s act only on the state $|n_s>$ but do not affect any other states because they are independent. The above equations justify the name of *creation and annihilation operators* for a_s^+ and a_s , respectively: a_s^+ creates a quantum in state s while a_s annihilates one quantum.

From (2.122,123) it is easily shown (Appendix E) that the individual matrix elements of a_s^+ and a_s are given by

$$\langle n'_s | a_s^+ | n_s \rangle = (n_s + 1)^{\frac{1}{2}} \delta_{n'_s, n_s+1} \quad (2.124)$$

$$\langle n'_s | a_s | n_s \rangle = n_s^{\frac{1}{2}} \delta_{n'_s, n_s-1} . \quad (2.125)$$

In addition, we show in Appendix E that the expectation values $\langle \dots n_s \dots | Q_s | \dots n_s \dots \rangle$ and $\langle \dots n_s \dots | P_s | \dots n_s \dots \rangle$ are zero [remember that s always stands for (qj)]. This is not surprising because a lattice wave involves only relative coordinates of the atoms except for the acoustic modes with $q = 0, \pm 2\pi/a, \pm 4\pi/a$, etc., which correspond to a translation of the chain as a whole. For this reason the total momentum vanishes. This can also be verified in classical mechanics by calculating the total momentum $p = \sum_{\ell K} p(\ell_K) = \sum_{\ell K} m_K \dot{u}(\ell_K)$. In this respect it is instructive to look at Fig.2.5 which gives the acoustic and optical modes of the diatomic NaCl chain for $q = 0$ and $q = \pi/a$. For the LA and TA modes at $q = 0$, the total momentum p is clearly different from zero, but for all other modes in Fig.2.5, $p = 0$. An analogous situation exists for vibrations in molecules: in an N_2 molecule, the internuclear vibrational coordinate $\vec{r}_1 - \vec{r}_2$ is a relative coordinate and

does not carry momentum; the center of mass coordinate $(1/2)(\vec{r}_1 + \vec{r}_2)$, however, corresponds to a uniform translational mode and can carry momentum.

2.2.4 Phonons

After having developed the formalism in Sect. 2.2.3, it is important to discuss its physical meaning. Formulas (2.122,123) can be interpreted in two equivalent ways (Fig. 2.9).

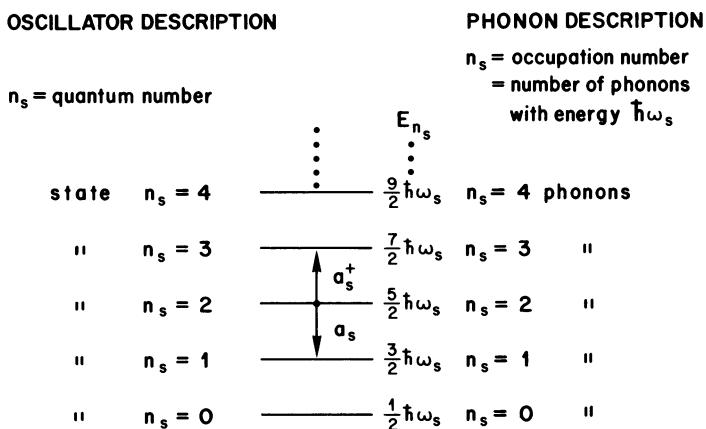


Fig. 2.9. Oscillator and phonon description of the vibrations of atoms in a crystal. The index s stands for (qj), where q is the wave number and j specifies the branch

a) The longitudinal vibrations of the diatomic linear chain are described in terms of $2N$ independent and distinguishable simple harmonic oscillators (Fig. 2.9); each oscillator is identified by an index $s = (qj)$, where q is its wave number and $j = 1, 2$ specifies the branch (LA or LO for longitudinal modes). The operator a_s^+ excites the oscillator s from the level n_s to the level $n_s + 1$ but does not affect all the other oscillators $s' \neq s$. Similarly, the operator a_s de-excites this oscillator only from the level n_s to the level $n_s - 1$.

b) In the second picture, the language of excited oscillators is replaced by an equivalent corpuscular description which is analogous to the terminology used in the quantum theory of the electromagnetic field. In that theory, the allowed energies of a normal mode of the radiation field in a cavity are given by $E_n = \hbar\omega(n + 1/2)$, where ω is the angular frequency of the mode. It

is common practice, however, to speak, not of the quantum number of excitations of the mode n , but of the number n of particles, called *photons*, with energy $\hbar\omega$.

Similarly, the allowed energies of a normal mode $s = (qj)$ of the displacement field are given by $E_{ns} = \hbar\omega_s(n_s + 1/2)$. Instead of saying that the oscillator s is in its n_s^{th} excited state, one says that there are $n_s = n_j(q)$ indistinguishable particles, called *phonons*, with wave number q and branch j in the system. n_s is called the *occupation number* of phonons in the state s (Fig.2.9), and the formalism developed in Sect.2.2.3 is known as the *occupation number representation*. In the harmonic approximation a phonon is considered to behave as a free particle, the wave function of which is given by $\psi(x,t) = \exp[i(\hbar/\lambda)(\hbar q x - \hbar\omega_s t)]$. The momentum operator is $p = -i\hbar\partial/\partial x$ and therefore, $p\psi = \hbar q\psi$. Thus, $\hbar q$ is the eigenvalue of the momentum operator p and q is the "quantum number" of the problem. $\hbar q$ is called the *quasimomentum* or *crystal momentum* of the phonon with quantum number q . Since, according to (2.32), q and $q' = q \pm (2\pi/a)$ describe the same mode of vibration, the quasimomentum $\hbar\vec{q}$ is defined only to within a vector $\vec{\tau} = (2\pi/a)\vec{e}$ of the reciprocal space; here \vec{e} is a unit vector. The name quasimomentum is due to this and the fact that, as discussed in Sect.2.2.3, a phonon does not really carry momentum since $\langle\psi|P|\psi\rangle = 0$. For this reason, the phonon is called a *quasi-particle*.

In the phonon picture, the relations (2.122,123) and (2.120) are interpreted in the following way: the creation operator a_s^+ creates an additional phonon in the state s while the annihilation operator a_s removes one (Fig. 2.9). According to the discussion given in Sect.2.2.3), a_s corresponds to the amplitude of the normal mode with wave number q , branch j , frequency $\omega_s = \omega_j(q)$ and intensity $a_s^+a_s$, the eigenvalue of which is the occupation number n_s .

The particle aspect of phonons is especially convenient if interactions between phonons and other particles such as photons, electrons, neutrons, or with other phonons are studied. In all these interactions in which one or several phonons are involved, the conservation of energy holds strictly but the conservation of momentum holds only to within a vector $\vec{\tau}$ of the reciprocal lattice. Processes with $\vec{\tau} = 0$ are called *normal processes* while processes for which $\vec{\tau} \neq 0$ are called *Umklapp processes*.

Phonons obey *Bose-Einstein statistics* and the total number of phonons is not conserved. For a system in equilibrium with a heat bath at temperature

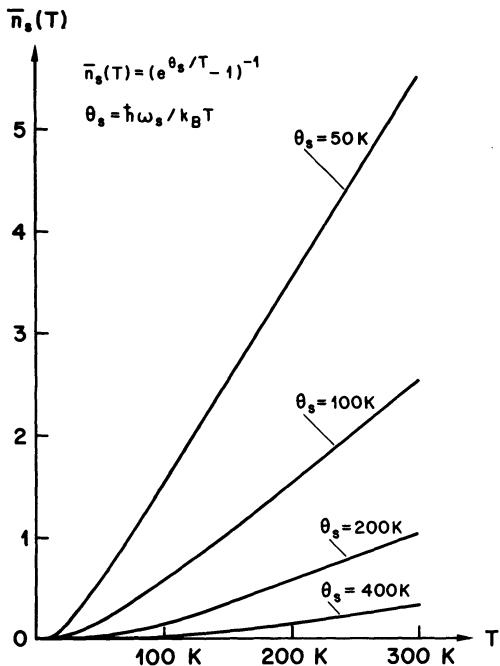


Fig. 2.10. Bose-Einstein distribution function giving the mean occupation number \bar{n}_s as a function of temperature T for different values of $\theta_s = \hbar\omega_s/k_B T$. The index s stands for (qj) , where q is the wave number and j specifies the branch. At low temperatures, only modes with low frequencies ω_s (small θ_s) are appreciably excited. Note that at high temperatures, \bar{n}_s is approximately linear in T .

T , the mean occupation number $\bar{n}_s(T) = \bar{n}_j(q, T)$ of phonons in the state $s = (qj)$ is given by the *Bose-Einstein distribution* [2.7]

$$\bar{n}_s(T) = [\exp(\hbar\omega_s/k_B T) - 1]^{-1} . \quad (2.126)$$

Figure 2.10 shows $\bar{n}_s(T)$ for different phonon frequencies $\omega_1 < \omega_2 < \omega_3$. At low temperatures, only low frequency phonons are appreciably excited and $\bar{n}_s(T) \approx \exp(-\hbar\omega_s/k_B T)$. With increasing temperature more and more phonons are excited and at high temperatures $\bar{n}_s(T) \approx k_B T/\hbar\omega_s$.

According to (2.102, 126), the mean energy of phonons in state $s = (qj)$ is given by

$$\bar{E}(\omega_s, T) = \hbar\omega_s \left\{ [\exp(\hbar\omega_s/k_B T) - 1]^{-1} + \frac{1}{2} \right\} \quad (2.127)$$

and according to (2.110), the total mean energy of the system is given by

$$\bar{E}(T) = \sum_s \bar{E}(\omega_s, T) . \quad (2.128)$$

At high temperatures we obtain the classical result (2.75), namely, $\bar{E} = 2Nk_B T$ for the longitudinal vibrations of the diatomic chain with N unit cells. We

also note that at $T = 0$ the system still has the "zero-point energy"

$$\bar{E}(T = 0) = \frac{1}{2} \sum_s \hbar\omega_s . \quad (2.129)$$

The system of phonons can thus be regarded as forming a gas of particles, called *phonon gas*. At low temperatures, the number of excited phonons is small and the interaction between the phonons is small due to the small density of particles in the gas. This low density phonon gas can be compared to an ideal gas in thermodynamics. The system of noninteracting phonons can be treated in the harmonic approximation. At higher temperatures, the number of phonons in the gas increases according to (2.126) and the interaction between the phonons becomes more important, a situation which can be compared with a real gas. Increasing interaction between the phonons means, of course, increasing anharmonicity.

2.2.5 Specific Heat and Density of States

The specific heat at constant volume is given by

$$c_V(T) = \frac{d\bar{E}(T)}{dT} , \quad (2.130)$$

where $\bar{E}(T)$ is given by (2.128) and (2.127), namely,

$$\bar{E}(T) = \sum_j \sum_q \bar{E}[\omega_j(q), T] \quad (2.131)$$

and

$$\bar{E}(\omega, T) = \hbar\omega \left\{ [\exp(\hbar\omega/k_B T) - 1]^{-1} + \frac{1}{2} \right\} . \quad (2.132)$$

When the number of unit cells N is large, as it must be in order for end effects of the chain to be negligible, it follows from (2.34) that the density of modes in the first Brillouin zone (BZ) becomes very high. Therefore, we can replace the sum over q in (2.131) by an integral over q . Introducing a density of state $\Gamma(q)$ in q -space such that $\Gamma(q)dq$ is the number of modes in the range dq and $\bar{E}(\omega_j(q), T)\Gamma(q)dq$ is the energy in that range, we obtain

$$\bar{E}(T) = \sum_j \int_{q \in BZ} \bar{E}[\omega_j(q), T] \Gamma(q) dq , \quad (2.133a)$$

where the integral extends over the first Brillouin zone (BZ).

Since according to (2.33-25) there are N different values in the range $2\pi/a$ of the first Brillouin zone which are uniformly distributed, we have

$$\Gamma(q) = \frac{Na}{2\pi} . \quad (2.134)$$

Since $\Gamma(q)$ is independent of q and $\omega_j(-q) = \omega_j(q)$, we can restrict the range of integration in (2.133a) to positive values of q in the first Brillouin zone and write

$$\bar{E}(T) = 2 \sum_j \int_{q>0} \bar{E}[\omega_j(q), T] \Gamma(q) dq . \quad (2.133b)$$

It is more convenient to transform (2.133b) into an integral over ω . We therefore introduce the frequency distribution $g_j(\omega_j)$ such that $g_j(\omega_j)d\omega_j$ is the number of modes (q_j) in the range $d\omega_j$. The relationship between $g_j(\omega_j)$ and $\Gamma(q)$ is clearly

$$g_j(\omega_j)d\omega_j = 2\Gamma(q)dq , \quad (2.135)$$

where we have again considered only positive values of q ; hence the factor 2 in (2.135). Substituting (2.135) in (2.133b), we obtain

$$\bar{E}(T) = \sum_j \int_{\omega_j} \bar{E}(\omega_j, T) g_j(\omega_j) d\omega_j . \quad (2.136)$$

This equation can also be written in the form

$$\bar{E}(T) = \int_0^{\omega_m} \bar{E}(\omega, T) g(\omega) d\omega , \quad (2.137)$$

where ω_m is some maximum frequency, $\bar{E}(\omega, T)$ is defined by (2.132) and

$$g(\omega) = \sum_j g_j(\omega) \quad (2.138)$$

is the total density of states. In fact, if we substitute (2.138) in (2.137) and replace the integration variable ω by ω_j , we obtain (2.136).

From (2.134,135), the frequency distribution is given by

$$g_j(\omega) = \frac{Na}{\pi} v_{gj}^{-1}(\omega) , \quad (2.139)$$

where

$$v_{gj}^{-1}(\omega) = \left| \frac{dq}{d\omega_j} \right|_{\omega_j=\omega} . \quad (2.140)$$

v_{gj} is the group velocity of the mode (q_j).

There is a normalizing condition for $g_j(\omega)$, namely, that the total number of modes of branch j is equal to N :

$$\int g_j(\omega) d\omega = N . \quad (2.141)$$

From (2.130,132,137), the specific heat is given by

$$c_V(T) = k_B \int \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp(\hbar\omega/k_B T) g(\omega)}{[\exp(\hbar\omega/k_B T) - 1]^2} d\omega . \quad (2.142)$$

If the density of states or the dispersion relation is known, $c_V(T)$ can, in principle, be calculated numerically from the relations (2.139-142) by using a computer. Even in simple cases such as the monoatomic or diatomic chain with nearest-neighbour interactions, for which the dispersion relations are given analytically by (2.44) and (2.14) or (2.36), respectively, the evaluation of the integrals must be performed numerically. Before introducing approximate distribution functions, we discuss the qualitative behaviour of $g_j(\omega)$ for the linear NaCl crystal [(2.36), Fig.2.4]. Since $g_j(\omega)$ is inversely proportional to $d\omega_j/dq$ and $d\omega_j/dq = 0$ for the acoustic and optic modes at $q = \pi/a$ and for the optic mode at $q = 0$, we obtain singularities in $g_1(\omega)$ at $\omega = \omega' = (2f/m_1)^{1/2}$ and in $g_2(\omega)$ at $\omega = \omega'' = (2f/m_2)^{1/2}$ and at $\omega = \omega_m = (2f/\mu)^{1/2}$. These singularities are known as *Van Hove singularities* [2.12] or *critical points*. The partial densities of states $g_1(\omega)$ (acoustic modes) and $g_2(\omega)$ (optic modes) are shown in Fig.2.11a.

The simplest approximation is the *Einstein model*, in which all the atoms oscillate independently with the same frequency ω_E , the *Einstein frequency*. In the Einstein model, each atom is bound by an elastic spring to its equilibrium position, but there are no interactions between different atoms. The dispersion relation for this model can symbolically be represented by a horizontal line and the corresponding density of states of the diatomic chain with $2N$ atoms is given by

$$g_E(\omega) = 2N\delta(\omega - \omega_E) \quad (2.143)$$

(see Fig.2.11b). The Einstein frequency is a mean frequency somewhere in the range between the acoustic and optical modes.

Next we consider the *Debye-model* which replaces the two longitudinal acoustic and optic branches with one branch given by

$$\omega = vq , \quad (2.144)$$

where $v = v(q = 0)$ is the *phase velocity* of the acoustic branch at $q = 0$ and is identical with the *velocity of sound*. According to Fig.2.11c, the optic branch of the spectrum is represented by the high q values of the same linear expression (2.144) whose low q values give the acoustic branch.

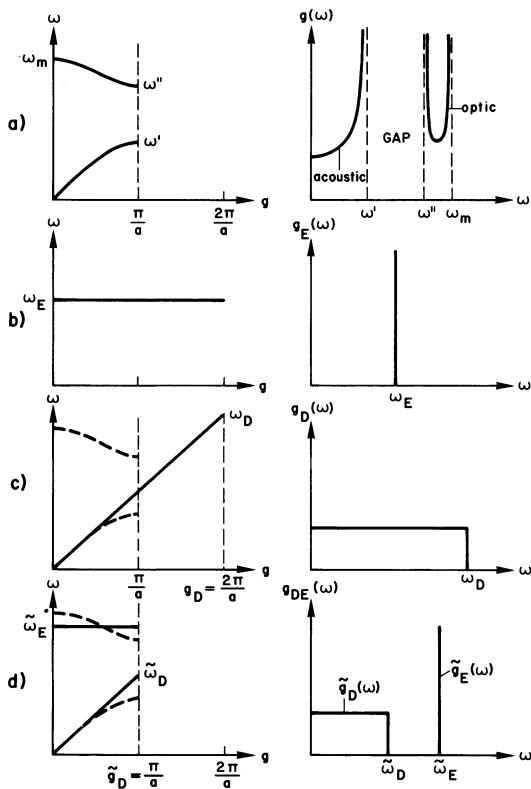


Fig. 2.11. Dispersion and densities of states for the acoustic and optic modes of the linear NaCl crystal. a) Qualitative behaviour for nearest-neighbour interactions; note the Van Hove singularities at the critical points ω' , ω'' and ω_m . b) Einstein model. c) Debye model. d) Hybride Einstein-Debye model

In this model, the group velocity v_g is identical with the phase velocity v and for the case of the linear NaCl crystal, we obtain from (2.37)

$$v = v(q=0) = v_{g1} = \left. \frac{d\omega_1}{dq} \right|_{q=0} = \left(\frac{f}{2(m_1 + m_2)} \right)^{\frac{1}{2}} a . \quad (2.145)$$

From (2.139,145), we obtain for the Debye-density of states

$$g_D(\omega) = \frac{Na}{\pi v} \quad (2.146)$$

independent of ω . Using the normalizing condition

$$\int_0^{\omega_D} g_D(\omega) d\omega = 2N , \quad (2.147)$$

we obtain from (2.146) for the Debye frequency

$$\omega_D = \frac{2\pi}{a} v \quad (2.148)$$

and $g_D(\omega)$ can be written in the form

$$g_D(\omega) = \begin{cases} 2N/\omega_D & \text{for } \omega < \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} . \quad (2.149)$$

We note that according to (2.144,148), the *Debye wave number* is given by

$$q_D = \frac{\omega_D}{v} = \frac{2\pi}{a} . \quad (2.150)$$

This situation is illustrated in Fig.2.11c.

An alternative scheme is to apply the Debye model only to the acoustic branch while the Einstein model represents the optical branch (Fig.2.11d). In this case, the density of states is given by

$$g_{DE}(\omega) = \tilde{g}_D(\omega) + \tilde{g}_E(\omega) , \quad (2.151)$$

where, as in (2.146), $\tilde{g}_D(\omega) = Na/\pi v$ but the normalizing condition is now

$$\int_0^{\omega_D} \tilde{g}_D(\omega) d\omega = N , \quad (2.152)$$

where $\tilde{\omega}_D = \omega_D/2$ and we obtain

$$\tilde{g}_D(\omega) = \begin{cases} N/\tilde{\omega}_D = 2N/\omega_D & \text{for } \omega < \tilde{\omega}_D \\ 0 & \text{for } \omega > \tilde{\omega}_D \end{cases} . \quad (2.153)$$

The Debye wave number is now given by

$$\tilde{q}_D = \frac{\tilde{\omega}_D}{v} = \frac{\pi}{a} = \frac{1}{2} q_D . \quad (2.154)$$

In this model, the Einstein density of states is

$$\tilde{g}_E(\omega) = N\delta(\omega - \tilde{\omega}_E) , \quad (2.155)$$

where $\tilde{\omega}_E$ is a mean optical vibration frequency.

This hybride model is illustrated in Fig.2.11d.

Substituting (2.143) in (2.142) and introducing the *Einstein temperature* θ_E by

$$k_B \theta_E = \hbar \omega_E , \quad (2.156)$$

we obtain for the *Einstein specific heat*

$$c_E(T) = 2Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2} . \quad (2.157)$$

At high temperatures ($T \gg \theta_E$), we obtain the classical result (2.76), namely, $c_E(T) = 2Nk_B$. At low temperatures ($T \ll \theta_E$), $c_E(T)$ drops exponentially according to

$$c_E(T) = 2Nk_B \left(\frac{\theta_E}{T}\right)^2 \exp(-\theta_E/T) \quad (T \ll \theta_E) . \quad (2.158)$$

This reflects the difficulty in thermally exciting optical modes at low temperatures. $c_E(T/\theta_E)$ is shown in Fig.2.12.

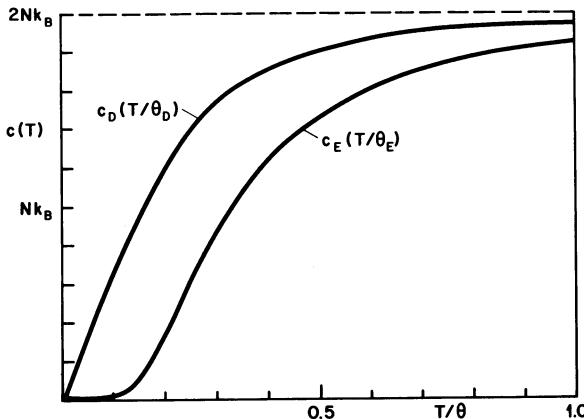


Fig.2.12. A comparison of the Einstein and Debye specific heat for longitudinal acoustic and optic branches of the linear NaCl crystal. θ is either the Einstein or the Debye temperature depending on which curve is being examined. Both curves are normalized to approach the classical value $2Nk_B$. For $T \ll \theta_E$, the specific heat $c_E(T)$ drops exponentially reflecting the difficulty in thermally exciting optical modes at low temperatures. $c_D(T)$ is linear at low temperatures; this is due to the thermal excitation of low frequency acoustic modes

Substituting (2.149) in (2.142) and defining the *Debye temperature* by

$$k_B \theta_D = \hbar \omega_D , \quad (2.159)$$

we obtain for the *Debye specific heat*

$$c_D(T) = 2Nk_B \frac{T}{\theta_D} \int_0^{\theta_D/T} \frac{x^2 e^x}{(e^x - 1)^2} dx , \quad (2.160)$$

where we have used the abbreviation $x = \hbar\omega/k_B T$.

At high temperatures, (2.160) again gives the classical result $c_D = 2Nk_B$ for the longitudinal vibrations of the diatomic chain. For the low temperature limit it is not permissible just to say $\hbar\omega/k_B T \gg 1$, since for small frequencies (acoustic modes at small q values) this condition cannot be satisfied. However, if $T \rightarrow 0$, $\theta_D/T \rightarrow \infty$ and the integral in (2.160) may be extended to infinity, in which case it has the value $\pi^2/3$. We obtain, therefore,

$$c_D(T) = 2 \frac{\pi^2}{3} N k_B \frac{T}{\theta_D} \quad (T \ll \theta_D) . \quad (2.161)$$

We note that in the Debye approximation, the specific heat of the linear chain is linear in T . $c_D(T/\theta_D)$ is represented in Fig. 2.12.

Substituting (2.151, 153, 155) in (2.142) and defining corresponding Debye and Einstein temperatures by $k_B \tilde{\theta}_D = \hbar \tilde{\omega}_D$ and $k_B \tilde{\theta}_E = \hbar \tilde{\omega}_E$, respectively, we obtain for the specific heat

$$c_{DE}(T) = N k_B \left\{ \frac{T}{\tilde{\theta}_D} \int_0^{\tilde{\theta}_D/T} \frac{x^2 e^x}{(e^x - 1)^2} dx + \left(\frac{\tilde{\theta}_E}{T} \right)^2 \frac{\exp(\tilde{\theta}_E/T)}{[\exp(\tilde{\theta}_E/T) - 1]^2} \right\} . \quad (2.162)$$

The specific heat now depends on two parameters, $\tilde{\theta}_D$ and $\tilde{\theta}_E$. At low temperatures, the specific heat is dominated by the Debye term and neglecting the Einstein contribution we obtain

$$c_{DE}(T) \approx \frac{\pi^2}{3} N k_B \frac{T}{\tilde{\theta}_D} \quad (T \ll \theta_D) . \quad (2.163)$$

Since $\tilde{\theta}_D = \theta_D/2$, the coefficient of T is exactly the same as in (2.161).

2.3 Problems

2.3.1 Monoatomic Chain

Consider a monoatomic chain of N unit cells with atoms of masses m , lattice parameter a and longitudinal displacements $u(\ell)$. The total force acting on atom ℓ is given by

$$F(\ell) = m\ddot{u}(\ell) = \sum_{p>0} f_p [u(\ell + p) + u(\ell - p) - 2u(\ell)] ,$$

where f_p is the force constant between atoms removed from each other by a distance pa . (Note that this model also describes elastic waves propagating in directions of high symmetry such as (100), (110) and (111) of monoatomic

cubic lattices, where entire planes of atoms move in phase and f_p are effective constants between these planes!)

a) Derive the dispersion relation $\omega(q)$ by considering a solution of the form (Sect.2.1.3)

$$u(\varrho) = (Nm)^{-\frac{1}{2}} |A(q)| \cos[q\varrho - \omega(q)t + \alpha(q)] .$$

b) Show that the same pattern of displacements is obtained for $q = \pi/6a$ ($\lambda = 12a$) and $q' = q + 2\pi/a$ ($\lambda' = 12a/13$). Draw a figure of the two waves for the case of transverse vibrations.

c) Using $\omega^2(q)$ from (a), derive the group velocity

$$v_g(q) = \frac{d\omega}{dq} = \frac{1}{2\omega} \frac{d\omega^2}{dq} .$$

d) Assuming nearest and second-nearest-neighbour interactions with $f_1 = f = 2f_2$, $f_p = 0$ for $p > 2$, plot the resulting dispersion $\omega(q)$.

e) Calculate the group velocity $v_g(q)$ and the phase velocity $v(q) = \omega(q)/|q|$ for nearest-neighbour interactions ($f_1 = f$, $f_p = 0$ for $p > 1$). Plot $v_g(q)$ in the range $-\pi/a \leq q \leq \pi/a$ and $v(q)$ in the range $-4\pi/a \leq q \leq 4\pi/a$.

f) Using the dispersion relation for nearest-neighbour interactions, calculate $q = q(\omega)$ and from this derive the expressions for $v_g(\omega)$ and $v(\omega)$. Plot these velocities in the range $-\pi/a \leq q \leq \pi/a$.

2.3.2 Chain with a Basis of Two Identical Atoms

Consider the chain shown in Fig.2.13 containing N unit cells with lattice parameter a and nearest-neighbour distances b and $a - b$ where $b < a - b$. Such a structure is a caricature of a hydrocarbon chain with alternating single and double bonds. If we put $m_1 = m_2 = m$ in the chain of Fig.2.1, we obtain the model considered here.

a) Using (2.14), plot the dispersion $\omega_{1,2}(q)$ for the LA branch ($j = 1$) and the LO branch ($j = 2$) in the first Brillouin zone.

b) Using (2.12,16,25,26), show that the components of the eigenvectors are

$$e(1|_j^q) = w_j(q)r_j(q), \quad e(2|_j^q) = w_j(q) ,$$

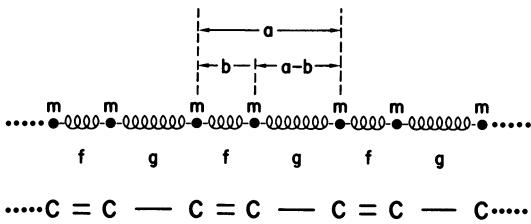


Fig.2.13. Linear chain with basis of two identical atoms of masses m and nearest-neighbour force constants f and g . a is the lattice parameter and $b < a - b$

where

$$r_j(q) = \frac{e^{iqb}(f + ge^{-iqa})}{f + g - m\omega_j^2(q)}$$

and

$$\omega_j(q) = (1 + |r_j(q)|^2)^{-\frac{1}{2}}.$$

Calculate $e(1|_j^q)$ and $e(2|_j^q)$ for $j = 1, 2$ and for $q = 0$ and π/a .

c) From (2.53) and the results obtained in (b), calculate the complex normal coordinates $Q(\frac{q}{j})$ for $q = 0$ and $q = \pi/a$.

Example:

$$Q(\frac{\pi/a}{1}) = (\frac{m}{2N})^{\frac{1}{2}} e^{-i\pi b/a} \sum_{\ell} (-1)^{\ell} [u(\frac{\ell}{1}) + u(\frac{\ell}{2})].$$

We have put $x(1) = 0$ and $x(2) = b$ in (2.53). Based on these normal coordinates, make a figure of the patterns of atomic displacements. Note that the displacements in $Q(\frac{\pi/a}{1})$ and $Q(\frac{\pi/a}{2})$ are such that only the bonds with force constants g and f , respectively, are changed.

d) From (2.62) and the results obtained in (c), express the real normal coordinates of the first kind, $\alpha_v(\frac{q}{j})$, in terms of the displacement coordinates $u(\frac{\ell}{k})$. Work out explicit expressions for $j = 1, 2$, $v = 1, 2$ and $q = 0$ and π/a .

e) From (2.67) and the results derived in (c), express the real normal coordinates of the second kind, $\eta(\frac{q}{j})$, in terms of the coordinates $u(\frac{\ell}{k})$ and the momenta $p(\frac{\ell}{k}) = m_k \dot{u}(\frac{\ell}{k})$. Note that $P(\frac{q}{j}) = \dot{Q}(\frac{q}{j})$. Work out explicit expressions for $j = 2$ and $q = 0$ and π/a .

2.3.3 Probability Densities of a Classical and Quantum Mechanical Oscillator

We derive the results shown in Fig.2.8b. We require that the classical oscillator has the same total energy E as the quantum mechanical oscillator in its ground state $n = 0$. From (2.79,84), we therefore have

$$E = \frac{1}{2} \hbar \omega = \frac{1}{2} (\dot{\eta}^2 + \omega^2 \eta^2) . \quad a)$$

Show that the classical probability density is

$$w_c(n) = \frac{1}{\pi \eta_0} (1 - n^2/\eta_0^2)^{-\frac{1}{2}} ,$$

where

$$\eta_0 = \gamma^{-\frac{1}{2}} = (\frac{\omega}{\hbar})^{-\frac{1}{2}} \text{ is the amplitude.}$$

Hint: The classical probability is

$$p_c(n) = \frac{dt(n)}{\frac{1}{2} T} = \frac{2}{T} \frac{dt(n)}{d\eta} d\eta = w_c(n) d\eta ,$$

where $dt(\eta)$ is the time the particle needs to pass from η to $\eta + d\eta$ and T is the period of oscillation ($\omega T = 2\pi$). Use (a) to calculate $dt/d\eta$ and the amplitude η_0 .

2.3.4 Density of States of the Monoatomic Chain with Nearest and Second-Nearest-Neighbour Interactions

Consider the dispersion $\omega(q)$ of the monoatomic chain of Problem 2.3.1d. Plot qualitatively the corresponding density of states. Note that there is a discontinuity at the zone boundary frequency $\omega_{ZB} = 2(f/m)^{\frac{1}{2}}$.

3. Dynamics of Three-Dimensional Crystals

In this chapter, we extend the results of the linear chain to three-dimensional crystals with n atoms in the primitive unit cell. We still use the harmonic approximation, where the forces acting on an atom when atoms are displaced from equilibrium positions are proportional to the displacements. This is only a good approximation if the displacements are very small compared with interatomic distances and as we have discussed in Sect.2.2.4, this will only be the case at sufficiently low temperatures and if the masses are not too small.

It is convenient to begin the theory of lattice dynamics of the three-dimensional crystal with the assumption of an indefinitely extended crystal. The absence of bounding surfaces results in a perfect lattice periodicity which greatly simplifies the theory. The assumption of an infinitely extended crystal, however, leads to infinite values of several quantities, such as the volume, energy, etc. In Sect.3.3, we shall introduce the Born-von Karman or periodic boundary conditions by which these quantities will be normalized to a finite value.

We start the discussion by formulating the Hamiltonian of the system and the equations of motion. The concept of force constants needs further examination before it can be applied in three dimensions. We shall discuss the restrictions on the atomic force constants which follow from infinitesimal translations of the whole crystal as well as from the translational symmetry of the crystal lattice. Next we introduce the dynamical matrix and the eigenvectors; this will be a generalization of Sect.2.1.2. In Sect.3.3, we introduce the periodic boundary conditions and give examples of Brillouin zones for some important structures. In strict analogy to Sect.2.1.4, we then introduce normal coordinates which allow the transition to quantum mechanics. All the quantum mechanical results which have been discussed in Sect.2.2 also apply for the three-dimensional case and only a summary of the main results is therefore given. We then discuss the den-

sity of states and the specific heat. In Sect.3.6 we study the connection of lattice dynamics with the theory of elasticity; we discuss the relationships between the elastic constants and the atomic force constants for Bravais lattices. The chapter ends with the applications of the lattice dynamics to monoatomic crystals with fcc structure.

3.1 Equations of Motion and Atomic Force Constants

We consider a crystal composed of an infinite number of unit cells, each of which is a parallelepiped defined by three noncoplanar vectors \vec{a}_1 , \vec{a}_2 and \vec{a}_3 (Fig.3.1). The equilibrium position vector of the ℓ^{th} unit cell relative to an origin located at some atom is denoted by [3.1]

$$\vec{r}(\ell) = \ell_1 \vec{a}_1 + \ell_2 \vec{a}_2 + \ell_3 \vec{a}_3 , \quad (3.1)$$

where ℓ_1 , ℓ_2 , ℓ_3 are any three integers, positive, negative, or zero which we will refer to collectively as ℓ . The vectors \vec{a}_1 , \vec{a}_2 , \vec{a}_3 are called the *primitive translation vectors* and they define the *primitive unit cell* which is the cell with the smallest volume from which the crystal structure can be generated by the translations of the lattice (3.1). If the primitive unit cell contains only one atom, the vector $\vec{r}(\ell)$ given by (3.1) defines the equilibrium positions of the atoms. Such crystals are called *Bravais* or *primitive* crystals. If there are $n > 1$ atoms in the primitive unit cell, this group of n atoms constitute the *basis* of the crystal structure. The equilibrium positions of the n atoms within the unit cell are given by the vectors $\vec{r}_{(\kappa)}$ with $\kappa = 1, \dots, n$. Thus, the equilibrium position of the κ^{th} atom in unit cell ℓ is given by

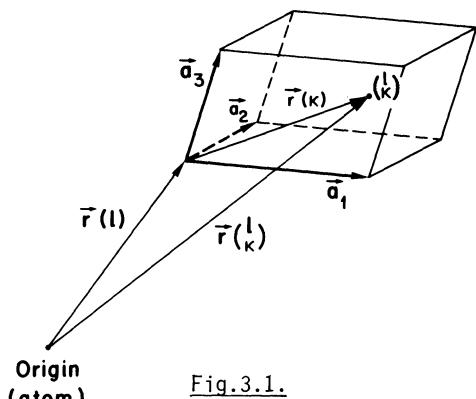
$$\vec{r}_{(\kappa)}^{(\ell)} = \vec{r}(\ell) + \vec{r}_{(\kappa)} . \quad (3.2)$$

As a result of thermal fluctuations, the atoms vibrate about their equilibrium positions and the actual position of the atom $(\kappa)^{(\ell)}$ is given by

$$\vec{R}_{(\kappa)}^{(\ell)} = \vec{r}_{(\kappa)}^{(\ell)} + \vec{u}_{(\kappa)}^{(\ell)} , \quad (3.3)$$

where $\vec{u}_{(\kappa)}^{(\ell)}$ is the displacement vector of the atom $(\kappa)^{(\ell)}$ from its equilibrium position $\vec{r}_{(\kappa)}^{(\ell)}$:

$$\vec{u}_{(\kappa)}^{(\ell)} = [u_x^{(\kappa)}(\ell), u_y^{(\kappa)}(\ell), u_z^{(\kappa)}(\ell)] . \quad (3.4)$$



Origin
(atom)

Fig. 3.1.

Definition of unit cell and equilibrium positions of atoms

In general, $u_\alpha(k)$ is the displacement of atom k in the direction α ($\alpha=x,y,z$).
The kinetic energy of the vibrating crystal is

$$T = \frac{1}{2} \sum_{\ell, \kappa, \alpha} m_\kappa \dot{u}_\alpha(k)^2 , \quad (3.5)$$

where m_κ is the mass of atom k . The potential energy Φ is assumed to be some function of the instantaneous positions of all atoms:

$$\Phi = \Phi[\dots \vec{r}(k) + \vec{u}(k) \dots] .$$

For small displacements, we can expand Φ about its equilibrium value using the three-dimensional form of Taylor's theorem:

$$\Phi = \Phi_0 + \sum_{\ell \kappa \alpha} \Phi_\alpha(k) u_\alpha(k) + \frac{1}{2} \sum_{\ell \kappa \alpha} \Phi_{\alpha \beta}(k k') u_\alpha(k) u_\beta(k') + \dots \quad (3.6)$$

In the harmonic approximation all cubic and higher-order terms are neglected. Since Φ_0 is just the static potential energy of the crystal (i.e., independent of the displacement coordinates), it can be ignored for the time being. The coefficients $\Phi_\alpha(k)$ and $\Phi_{\alpha \beta}(k k')$ are defined by

$$\Phi_\alpha(k) = \left[\frac{\partial \Phi}{\partial u_\alpha(k)} \right]_0 \quad (3.7)$$

$$\Phi_{\alpha \beta}(k k') = \left[\frac{\partial^2 \Phi}{\partial u_\alpha(k) \partial u_\beta(k')} \right]_0 , \quad (3.8)$$

where the subscript zero means that the derivatives are evaluated in the equilibrium configuration defined by (3.2). We shall see below that for the

special elements $\Phi_{\alpha\beta}^{(\ell\ell)}(KK)$, the definition (3.8) must be modified, see (3.17b). The force acting on the atom (ℓ_K) in the α -direction due to the displacements of all atoms $(\ell'_{K'})$ is given by

$$F_\alpha^{(\ell)} = - \frac{\partial \Phi}{\partial u_\alpha^{(\ell)}} . \quad (3.9)$$

From (3.6) we obtain

$$F_\alpha^{(\ell)} = - \Phi_\alpha^{(\ell)} - \sum_{\ell' K' \beta} \Phi_{\alpha\beta}^{(\ell\ell')} u_\beta^{(\ell')} - \dots \quad (3.10)$$

Suppose that all atoms are in their equilibrium positions, that is, all displacements $u_\beta^{(\ell')}$, are zero. In this case, we obtain the force $F_\alpha^{(\ell)}|_0$ = $- \Phi_\alpha^{(\ell)}$ from (3.10). However, by definition of the equilibrium, this force must be zero and therefore

$$\Phi_\alpha^{(\ell)} = 0 . \quad (3.11)$$

In the harmonic approximation, we obtain

$$F_\alpha^{(\ell)} = - \sum_{\ell' K' \beta} \Phi_{\alpha\beta}^{(\ell\ell')} u_\beta^{(\ell')} \quad (3.12)$$

from (3.10,11) for the force acting on the atom (ℓ_K) in the α -direction and from (3.6,11), the potential energy is given by

$$\Phi = \frac{1}{2} \sum_{\ell K \alpha} \Phi_{\alpha\beta}^{(\ell\ell')} u_\alpha^{(\ell)} u_\beta^{(\ell')} . \quad (3.13)$$

The Hamilton function for the crystal in the harmonic approximation follows from (3.5,13):

$$H = \frac{1}{2} \sum_{\ell K \alpha} m_K \dot{u}_\alpha^2(\ell_K) + \frac{1}{2} \sum_{\ell K \alpha} \Phi_{\alpha\beta}^{(\ell\ell')} u_\alpha^{(\ell)} u_\beta^{(\ell')} . \quad (3.14)$$

From (3.12) we immediately obtain the equations of motion

$$m_K \ddot{u}_\alpha^{(\ell)} = - \sum_{\ell' K' \beta} \Phi_{\alpha\beta}^{(\ell\ell')} u_\beta^{(\ell')} . \quad (3.15)$$

The coefficients $\Phi_{\alpha\beta}^{(\ell\ell')}$ are called *atomic force constants*. In the harmonic approximation, these force constants have a very simple physical meaning. Suppose all atoms are at their equilibrium positions except the atom $(\ell'_{K'})$ which is displaced a unit distance d_β in the β -direction. In this case, we obtain from (3.12)

$$F_{\alpha}(\ell) = - \Phi_{\alpha\beta}(\ell\ell') d_{\beta} .$$

From this it follows that the coefficient $\Phi_{\alpha\beta}(\ell\ell')$ is the negative force exerted in the α -direction on the atom (ℓ) when the atom (ℓ') is displaced a unit distance in the β -direction, while all other atoms are kept at their equilibrium positions (Fig.3.2). In the definition (3.8) of the force constants, we can interchange the order of differentiation without changing the value of the force constants. Therefore, the force constants satisfy the following symmetry condition:

$$\Phi_{\alpha\beta}(\ell\ell') = \Phi_{\beta\alpha}(\ell'\ell) . \quad (3.16)$$

In the following, we derive additional relations between the force constants which follow from the invariance of the potential energy against infinitesimal translations of the crystal as a whole, as well as against the discrete translations of the crystal lattice.

We can describe a rigid body translation of the crystal by replacing each displacement $u_{\beta}(\ell')$ in (3.12) by an arbitrary constant v_{β} . It is clear that for such a translation of the whole crystal the force $F_{\alpha}(\ell)$ must vanish, that is, we obtain

$$\sum_{\beta} v_{\beta} \sum_{\ell' \neq \ell} \Phi_{\alpha\beta}(\ell\ell') = 0 ,$$

and since the constants v_{β} are arbitrary, we obtain

$$\sum_{\ell' \neq \ell} \Phi_{\alpha\beta}(\ell\ell') = 0 . \quad (3.17a)$$

From this relation it follows that $\Phi_{\alpha\beta}(\ell\ell')$ is not the second derivative of Φ with respect to $u_{\alpha}(\ell)$ but is given by

$$\Phi_{\alpha\beta}(\ell\ell') = - \sum_{(\ell') \neq (\ell)} \Phi_{\alpha\beta}(\ell\ell') . \quad (3.17b)$$

This relation will be useful for many applications.

Next, we suppose that we subject our infinite crystal to a lattice translation $\vec{t}(m) = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$, where m_i are integers and \vec{a}_i are the primitive translation vectors. Such a translation transforms the atom (ℓ) into the atom $(\ell+m)$ and the atom (ℓ') into the atom $(\ell'+m)$ and we expect that

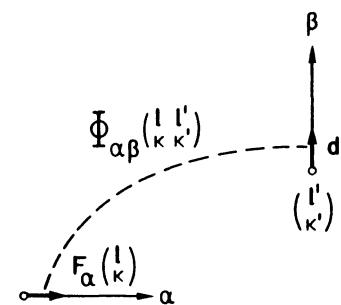


Fig. 3.2.
Definition of the coupling coefficients $\Phi_{\alpha\beta}^{(l l' k k')}$

$$\Phi_{\alpha\beta}^{(l+m \ l'+m \ k \ k')} = \Phi_{\alpha\beta}^{(l l' \ k \ k')} . \quad (3.18)$$

The rigorous mathematical proof of (3.18) is given in Appendix F and is based on the fact that the potential energy Φ is invariant against such lattice translations. If $m = -l$, we obtain from (3.18)

$$\Phi_{\alpha\beta}^{(l l' \ k k')} = \Phi_{\alpha\beta}^{(0 \ l' - l \ k \ k')}$$

and if $m = -l'$, we obtain

$$\Phi_{\alpha\beta}^{(l l' \ k k')} = \Phi_{\alpha\beta}^{(l - l' \ 0 \ k \ k')} .$$

Thus, the force constants depend on l and l' only through their difference and we can write

$$\begin{aligned} \Phi_{\alpha\beta}^{(l l' \ k k')} &= \Phi_{\alpha\beta}^{(0 \ l' - l \ k \ k')} \\ &= \Phi_{\alpha\beta}^{(l - l' \ 0 \ k \ k')} . \end{aligned} \quad (3.19)$$

In Appendix F, additional relations between the force constants are derived which are due to the invariance of Φ against the symmetry elements of the space group of the crystal.

3.2 Dynamical Matrix and Eigenvectors

We consider a solution to the equations of motion (3.15) of the following form:

$$u_\alpha^{(l)} = \frac{1}{2} (Nm_k)^{-\frac{1}{2}} \left\{ A(q) e_\alpha(k|\vec{q}) \exp\{i[\vec{qr}_k^l - \omega(\vec{q})t]\} + c.c. \right\} , \quad (3.20)$$

where c.c. means the conjugate complex of the first term in the curly brackets of (3.20). The analogous solution for the diatomic linear chain is given by (2.7b). $A(\vec{q})$ and $e_\alpha(\kappa|\vec{q})$ are amplitudes which are defined by equations analogous to (2.9,10). The solution (3.20) describes a plane wave travelling parallel to the wave vector \vec{q} . Substituting this solution into (3.15), one finds after separating out terms of the same time dependence and cancellation of common factors

$$\omega^2(\vec{q})e_\alpha(\kappa|\vec{q}) = \sum_{\kappa' \beta} D_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) e_\beta(\kappa'|\vec{q}) , \quad (3.21)$$

where the elements of the dynamical matrix $D(\vec{q})$ are given by

$$D_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) = (m_\kappa m_{\kappa'})^{-\frac{1}{2}} \sum_{\ell} \Phi_{\alpha\beta}(\ell\ell') \exp\{i\vec{q}[\vec{r}(\ell') - \vec{r}(\ell)]\} . \quad (3.22)$$

Using (3.1,2,19) and the abbreviation $L = \ell' - \ell$, we can rewrite (3.22) in the form

$$D_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) = \frac{\exp\{i\vec{q}[\vec{r}(\kappa') - \vec{r}(\kappa)]\}}{(m_\kappa m_{\kappa'})^{\frac{1}{2}}} \sum_L \Phi_{\alpha\beta}(0 L) e^{i\vec{q}\vec{r}(L)} . \quad (3.23)$$

This form shows explicitly that the elements of the dynamical matrix $D(\vec{q})$ depend only on the difference $L = \ell' - \ell$ and are therefore independent of ℓ . The dimension of the dynamical matrix is $3n$, where n is the number of atoms in the primitive unit cell ($\alpha, \beta = x, y, z; \kappa, \kappa' = 1 \dots n$). We have, therefore, reduced the infinite set of equations of motion (3.15) to the problem (3.21) which represents a set of $3n$ linear homogeneous equations in the $3n$ unknown amplitudes $e_\alpha(\kappa|\vec{q})$ for each wave vector \vec{q} . This reduction is a direct consequence of the periodicity of the lattice as expressed by (3.19).

Equation (3.21) can be rewritten as

$$\sum_{\kappa' \beta} [D_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) - \delta_{\alpha\beta} \delta_{\kappa\kappa'} \omega^2(\vec{q})] e_\beta(\kappa'|\vec{q}) = 0 . \quad (3.24)$$

The condition that the homogeneous system of equations (3.24) have a non-trivial solution is that the determinant of the coefficients vanish [3.2]

$$|D_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) - \delta_{\alpha\beta} \delta_{\kappa\kappa'} \omega^2(\vec{q})| = 0 . \quad (3.25)$$

Equation (3.25) is an equation of $3n^{\text{th}}$ degree in $\omega^2(\vec{q})$ and the $3n$ solutions for each value of \vec{q} will be denoted by $\omega_j^2(\vec{q})$ where $j = 1, 2 \dots 3n$. In Appendix G we show that $D(\vec{q})$ is a Hermitian matrix, that is,

$$D^+(\vec{q}) = D^{*T}(\vec{q}) = D(\vec{q}) \quad , \quad (3.26)$$

where D^{*T} is the transposed and complex conjugate matrix of D . An example of a Hermitian matrix $D(q)$ is given by (2.12) for the diatomic linear chain. The fact that $D(\vec{q})$ is Hermitian implies that the eigenvalues $\omega_j^2(\vec{q})$ are real [3.2], so that $\omega_j(\vec{q})$ is either real or purely imaginary. From (3.20) we see that if $\omega_j(\vec{q})$ was purely imaginary, this would imply a motion of the lattice which erupts exponentially either into the past or into the future. Therefore, the microscopic condition for the stability of the lattice is that each $\omega_j^2(\vec{q})$ be positive (or zero). The relation expressed by the equation $\omega = \omega_j(\vec{q})$ for $j = 1 \dots 3n$ is known as the *dispersion relation*. Dispersion relations for the diatomic chain have been derived in Chap.2, (2.14).

If we substitute an eigenvalue $\omega_j^2(\vec{q})$ in (3.24), we obtain corresponding amplitudes $e_\beta(\kappa|\vec{q}_j)$ and (3.21) can now be written in the form

$$\sum_{\kappa' \beta} D_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) e_\beta(\kappa'|\vec{q}_j) = e_\alpha(\kappa|\vec{q}_j) \omega_j^2(\vec{q}) \quad . \quad (3.27)$$

This equation shows that the $3n$ amplitudes $e_\beta(\kappa|\vec{q}_j)$ ($\beta = 1, 2, 3$; $\kappa = 1 \dots n$) are the components of an *eigenvector* $\vec{e}(\vec{q}_j)$ of $D(\vec{q})$ which belongs to the eigenvalue $\omega_j^2(\vec{q})$. Just as for the case of the diatomic chain [(2.17,23)], we can write (3.27) in matrix form

$$D(\vec{q})e(\vec{q}) = e(\vec{q})\Lambda(\vec{q}) \quad , \quad (3.28a)$$

$$D(\vec{q})\vec{e}(j) = \lambda_j(\vec{q})\vec{e}(j) \quad , \quad (3.28b)$$

where $\lambda_j(\vec{q}) = \omega_j^2(\vec{q})$. The $3n$ -dimensional matrices $D(\vec{q})$, $e(\vec{q})$ and $\Lambda(\vec{q})$ have the following form:

$$D(q) = \begin{array}{c} \uparrow \\ \kappa \alpha \\ \downarrow \end{array} \left[\begin{array}{ccc} & \leftarrow \kappa' \beta & \rightarrow \\ & \vdots & \\ \dots & D_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) & \dots \\ & \vdots & \end{array} \right]$$

$$e(\vec{q}) = \begin{array}{c} \uparrow \\ \kappa' \beta \\ \downarrow \end{array} \left[\begin{array}{ccc} & \leftarrow j & \rightarrow \\ & \vdots & \\ \dots & e_\beta(\kappa'|\vec{q}_j) & \dots \\ & \vdots & \end{array} \right]$$

$$\vec{\Lambda}(\vec{q}) = \begin{bmatrix} & & + j' & + \\ & \omega_1^2(\vec{q}) & & \\ & . & 0 & \\ & . & \omega_j^2(\vec{q}) & \\ & 0 & . & \omega_{3n}^2(\vec{q}) \\ & & & \end{bmatrix}$$

The columns of $e(\vec{q})$ are the eigenvectors $\vec{e}_j(\vec{q})$.

Equation (3.24) defines the amplitudes $e_\alpha(\kappa|\vec{j})$ to within a constant factor and in strict analogy to (2.25,26), we can choose this factor in such a way that the $e_\alpha(\kappa|\vec{j})$ satisfy the orthonormality and closure conditions

$$\sum_{\kappa\alpha} e_\alpha^*(\kappa|\vec{j}) e_\alpha(\kappa|\vec{j}') = \delta_{jj'} , \quad (3.29)$$

$$\sum_j e_\alpha(\kappa|\vec{j}) e_\beta^*(\kappa'|\vec{j}) = \delta_{\alpha\beta} \delta_{\kappa\kappa'} . \quad (3.30)$$

Furthermore, by considerations paralleling those for the diatomic chain (2.27-31), we obtain the result

$$e_\alpha^*(\kappa|\vec{j}) = e_\alpha(\kappa|\vec{j}) . \quad (3.31)$$

From (3.27) and (3.17a) it can be shown (Appendix H) that of the $3n$ solutions $\omega_j^2(\vec{q})$ for each value of \vec{q} , three go to zero as \vec{q} goes to zero. These are the *acoustic modes*, which for $\vec{q} = 0$ correspond to translations of the crystal in the directions $\alpha = x, y, z$. The remaining $3n - 3$ modes are the *optical modes*. The character of these modes have been discussed in detail for the case of the diatomic linear chain [(2.37-40); Figs.2.5,6].

At the beginning of this section we considered the solution (3.20), namely,

$$u_\alpha(\ell) = \frac{1}{2} (Nm_\kappa)^{-\frac{1}{2}} \left(A(\vec{q}) e_\alpha(\kappa|\vec{q}) \exp\{i[\vec{qr}(\ell) - \omega(\vec{q})t]\} + c.c. \right) .$$

It is, of course, also possible to write the solution in the form

$$u_\alpha(\ell) = \frac{1}{2} (Nm_\kappa)^{-\frac{1}{2}} \left(A(\vec{q}) \tilde{e}_\alpha(\kappa|\vec{q}) \exp\{i[\vec{qr}(\ell) - \omega(\vec{q})t]\} + c.c. \right) . \quad (3.20a)$$

In the representation (3.20a), the elements of the dynamical matrix are

$$\tilde{D}_{\alpha\beta}(\vec{q}) = (m_{\kappa\kappa'})^{-\frac{1}{2}} \sum_{\ell'} \Phi_{\alpha\beta}(\ell\ell') \exp[i\vec{q}[\vec{r}(\ell') - \vec{r}(\ell)]], \quad (3.22a)$$

instead of (3.22). The matrices $D(\vec{q})$ and $\tilde{D}(\vec{q})$ have the same eigenvalues and the relation between the components of the eigenvectors is

$$\tilde{e}_\alpha(\kappa|\vec{q}) = e^{i\vec{q}\vec{r}(\kappa)} e_\alpha(\kappa|\vec{q}). \quad (3.32)$$

The components $\tilde{e}_\alpha(\kappa|\vec{q})$ satisfy relations analogous to (3.29,30). An advantage of the choice (3.20) is that for crystals such as the alkali halides where each atom is at a centre of symmetry, $D(\vec{q})$ and $e(\vec{q})$ are real matrices.

3.3 Periodic Boundary Conditions, Reciprocal Lattices and Brillouin Zones

We started our discussion in this chapter by assuming an infinitely extended crystal. Now we shall introduce the Born-von Karman or periodic boundary conditions as we did for the linear chain in Chap.2. For this purpose we subdivide the infinitely large crystal into "macrocrystals". Each macrocrystal is a parallelepiped defined by the vectors $N_1\vec{a}_1$, $N_2\vec{a}_2$, $N_3\vec{a}_3$, where \vec{a}_1 , \vec{a}_2 , \vec{a}_3 are the primitive translation vectors and N_1 , N_2 , N_3 are large integers. Each macrocrystal contains $N = N_1N_2N_3$ primitive unit cells and can be regarded as the physical crystal whose vibrational properties we are studying (Fig.3.3).

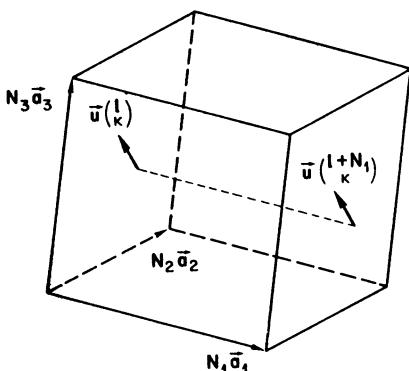


Fig.3.3. Definition of a macrocrystal and illustration of the Born-von Karman periodic boundary conditions

The periodic boundary conditions require that the atomic displacements for atoms separated by a translation $N_i\vec{a}_i$, or a sum of such translations, must be the same

$$\vec{u}(\kappa^{\ell+N_i}) = \vec{u}(\kappa^\ell) \quad (3.33)$$

for $i = 1, 2, 3$ (Fig.3.3). These conditions are a natural generalization of the periodic boundary conditions for the linear chain illustrated in Fig.2.3. Replacing ℓ by $\ell + N_i$ in (3.20) and observing that $\vec{r}(\kappa^{\ell+N_i}) = \vec{r}(\kappa^\ell) + N_i \vec{a}_i$, we obtain from the condition (3.33)

$$\exp(i\vec{q}N_i \vec{a}_i) = 1 \quad . \quad (3.34)$$

Equation (3.34) specifies the possible values of \vec{q} . In order to express these conditions in a simple manner, we introduce the *reciprocal lattice*. The primitive translation vectors of the reciprocal lattice are the three vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$ defined by [3.1]

$$\vec{a}_i \vec{b}_j = 2\pi \delta_{ij} \quad . \quad (3.35)$$

These equations can be satisfied by putting

$$\begin{aligned} \vec{b}_1 &= \frac{2\pi}{v_a} (\vec{a}_2 \times \vec{a}_3) \\ \vec{b}_2 &= \frac{2\pi}{v_a} (\vec{a}_3 \times \vec{a}_1) \\ \vec{b}_3 &= \frac{2\pi}{v_a} (\vec{a}_1 \times \vec{a}_2) \quad , \end{aligned} \quad (3.36)$$

where

$$v_a = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) \quad (3.37)$$

is the volume of the primitive unit cell of the direct lattice. A lattice vector in the reciprocal lattice is given by

$$\vec{r}(n) = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3 \quad , \quad (3.38)$$

where the n_i are arbitrary integers which can be positive, negative or zero. Using (3.36), we obtain for the scalar product between a direct lattice vector $\vec{r}(\ell) = \ell_1 \vec{a}_1 + \ell_2 \vec{a}_2 + \ell_3 \vec{a}_3$ and a reciprocal lattice vector

$$\vec{r}(\ell) \cdot \vec{r}(n) = 2\pi \sum_i \ell_i n_i = 2\pi \times (\text{integer}) \quad . \quad (3.39)$$

From (3.35) it follows that an expression for \vec{q} which satisfies (3.34) is given by

$$\vec{q} = \frac{n_1}{N_1} \vec{b}_1 + \frac{n_2}{N_2} \vec{b}_2 + \frac{n_3}{N_3} \vec{b}_3 . \quad (3.40a)$$

Now, we show in Appendix A that for the diatomic linear chain, the eigenvalues and the atomic displacements are periodic functions of $\tau = 2\pi m/a$. The extension of the results to the general three-dimensional case is straightforward and gives

$$\omega_j(\vec{q} + \vec{\tau}) = \omega_j(\vec{q}) \quad (3.41)$$

and

$$\vec{u}_{\kappa j}^{(\ell)}(\vec{q} + \vec{\tau}) = \vec{u}_{\kappa j}^{(\ell)}(\vec{q}) . \quad (3.42)$$

Therefore, we obtain all distinct solutions to our problem if we restrict the allowed values of \vec{q} to lie in one unit cell of the reciprocal lattice defined by the three vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$. This means that the integers n_i in (3.40a) are restricted to

$$n_i = 0, 1, 2, \dots N_i - 1$$

or

$$n_i = 1, 2, \dots N_i . \quad (3.40b)$$

The unit cell defined by $\vec{b}_1, \vec{b}_2, \vec{b}_3$ does not, in general, reflect the symmetry of the reciprocal lattice. It is, however, always possible to construct a primitive unit cell in such a way that the point symmetry of the reciprocal lattice is in evidence. This can be achieved by the following rule: starting from a point (call it $\vec{q} = 0$) in the reciprocal lattice, one constructs vectors to neighbouring points of the reciprocal lattice and bounds the unit cell by planes which are perpendicular bisectors of the vectors to the neighbouring points. Such a cell is called the *Brillouin zone* [3.3]. The analogous construction in real space defines the *Wigner-Seitz cell* [3.4,5]. The volume of the Brillouin zone is the same as the volume of the primitive unit cell defined by $\vec{b}_1, \vec{b}_2, \vec{b}_3$ and is given by

$$v_b = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{v_a} , \quad (3.43)$$

where we have used (3.36) and v_a is given by (3.37). According to (3.40a, 3.40b) the allowed values of \vec{q} are distributed uniformly in reciprocal space and each unit cell of the reciprocal lattice contains $N = N_1 N_2 N_3$ distinct values of \vec{q} which equals the number of primitive unit cells in the macrocrystal shown in Fig.3.3. Hence, the density of states of the values

of \vec{q} is given by

$$r(\vec{q}) = \frac{N}{V_b} = \frac{Nv_a}{(2\pi)^3} = \frac{V}{(2\pi)^3} \quad , \quad (3.44)$$

where V is the volume of the macocrystal. Thus, $r(\vec{q})$ is independent of \vec{q} ; the analogous density for the linear chain is given by (2.134).

For further reference, we illustrate the Brillouin zones of some simple and important structures. The CsCl structure is shown in Fig.3.4a. The lattice vectors are

$$\vec{a}_1 = a(1, 0, 0); \vec{a}_2 = (0, 1, 0), \vec{a}_3 = a(0, 0, 1) \quad , \quad (3.45)$$

and according to (3.36), the reciprocal lattice vectors are

$$\vec{B}_1 = \frac{2\pi}{a}(1, 0, 0); \vec{B}_2 = \frac{2\pi}{a}(0, 1, 0), \vec{B}_3 = \frac{2\pi}{a}(0, 0, 1) \quad . \quad (3.46)$$

Figure 3.4b shows the Brillouin zone for this case which is a cube. Points of special interest corresponding to special \vec{q} -values are labelled following a widely used convention introduced by BOUCKAERT et al. [3.6].

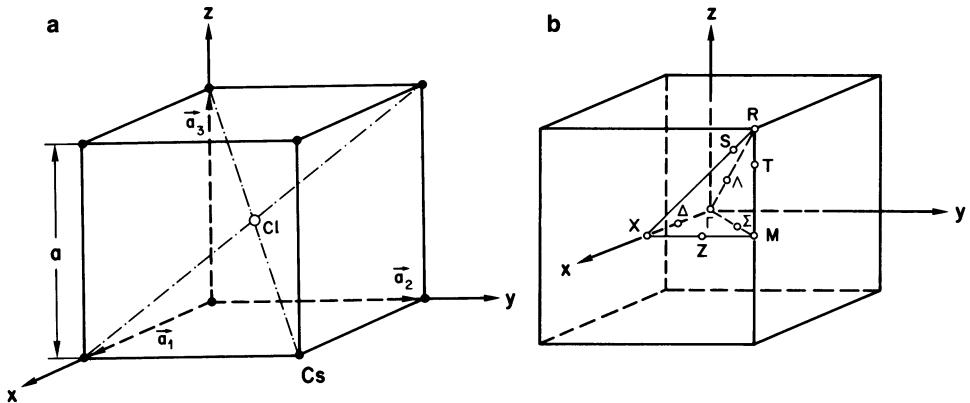


Fig.3.4. a) Unit cell and primitive translation vectors of the CsCl structure. b) Brillouin zone of the CsCl structure [3.5]

In Figure 3.5, the body-centered-cubic (bcc) lattice and the corresponding Brillouin zone are illustrated. The primitive translation vectors are

$$\vec{a}_1 = \frac{a}{2}(1, 1, -1), \vec{a}_2 = \frac{a}{2}(-1, 1, 1), \vec{a}_3 = \frac{a}{2}(1, -1, 1) \quad (3.47)$$

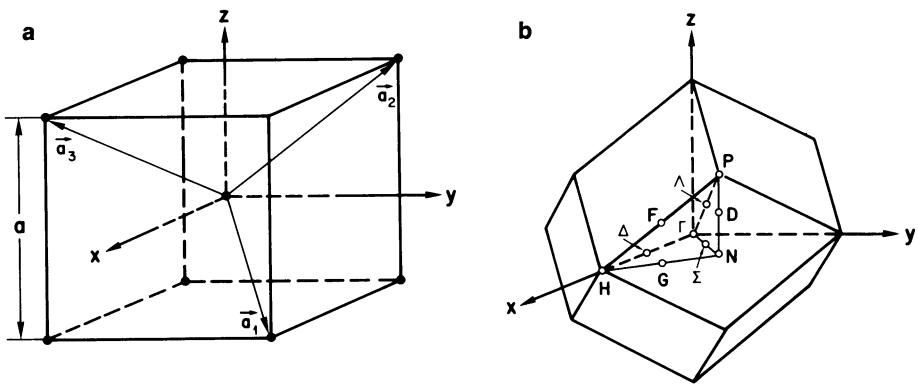


Fig.3.5. a) Unit cell and primitive translation vectors of the body centered cubic (bcc) lattice. b) Brillouin zone of the bcc lattice [3.5]

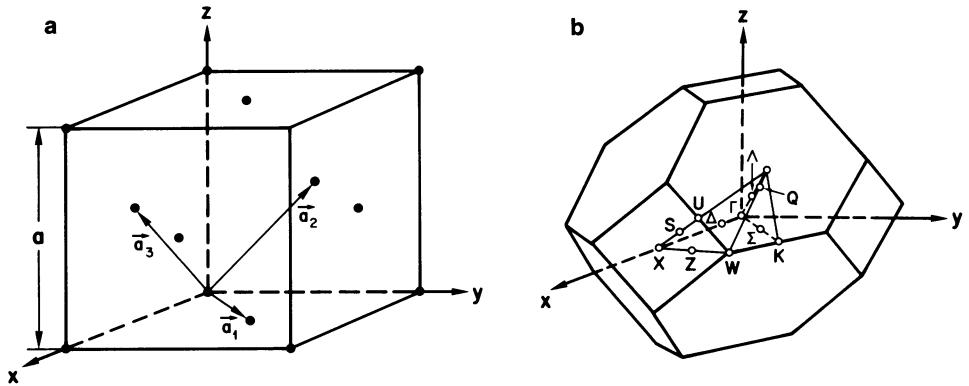


Fig.3.6. a) Unit cell and primitive translation vectors of the face-centered-cubic (fcc) lattice. b) Brillouin zone of the fcc lattice

and the volume of the primitive unit cell is $v_a = a^3/2$. From (3.36) we obtain

$$\vec{b}_1 = \frac{2\pi}{a} (1, 1, 0), \vec{b}_2 = \frac{2\pi}{a} (0, 1, 1), \vec{b}_3 = \frac{2\pi}{a} (1, 0, 1) . \quad (3.48)$$

In Fig.3.6, the face-centered-cubic (fcc) lattice and the corresponding Brillouin zone are exhibited. This applies, for example, to NaCl. The primitive translation vectors are

$$\vec{a}_1 = \frac{a}{2} (1, 1, 0), \vec{a}_2 = \frac{a}{2} (0, 1, 1), \vec{a}_3 = \frac{a}{2} (1, 0, 1) \quad (3.49)$$

and the volume of the rhombohedral unit cell is $v_a = a^3/4$. The reciprocal lattice vectors are given by

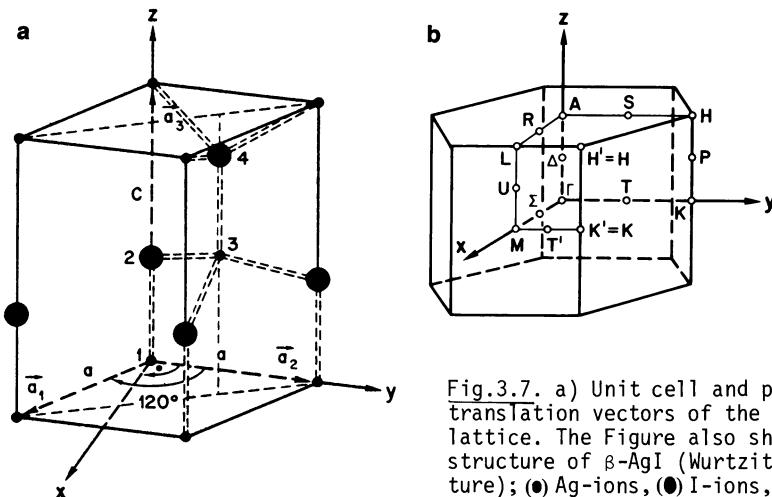


Fig.3.7. a) Unit cell and primitive translation vectors of the hexagonal lattice. The Figure also shows the structure of β -AgI (Wurtzite structure); (●) Ag-ions, (○) I-ions, (---) Ag-I bonds; ions number 1 to 4 belong to the unit cell. b) Brillouin zone of the hexagonal lattice [3.5]

$$\vec{b}_1 = \frac{2\pi}{a} (1, 1, -1), \vec{b}_2 = \frac{2\pi}{a} (-1, 1, 1), \vec{b}_3 = \frac{2\pi}{a} (1, -1, 1) . \quad (3.50)$$

Finally, we consider the hexagonal unit cell shown in Fig.3.7a. The primitive translation vectors are

$$\vec{a}_1 = a \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0 \right), \vec{a}_2 = a(0, 1, 0), \vec{a}_3 = c(0, 0, 1) \quad (3.51)$$

and the volume of the unit cell is $v_a = (\sqrt{3}/2)a^2c$. The reciprocal lattice vectors are

$$\vec{b}_1 = \frac{4\pi}{\sqrt{3}a} (1, 0, 0), \vec{b}_2 = \frac{4\pi}{\sqrt{3}a} \left(\frac{1}{2}, \sqrt{3}/2, 0 \right), \vec{b}_3 = \frac{2\pi}{c} (0, 0, 1) . \quad (3.52)$$

The Brillouin zone is shown in Fig.3.7b.

3.4 Normal Coordinates, Phonons

The generalization of the results derived for the diatomic chain (Sects. 2.1.4, 2.2.2-4) to the general three-dimensional crystal is trivial. It is only necessary to replace the scalar quantities q , $u(\frac{k}{\lambda})$, $x(\frac{k}{\lambda})$, $e(k|j^q)$ by the corresponding three-dimensional vectors \vec{q} , $\vec{u}(\frac{k}{\lambda})$, $\vec{x}(\frac{k}{\lambda})$, $\vec{e}(k|j^q)$. For later reference, we summarize in this section the most important results.

The *normal coordinates* $Q(\vec{q}_j)$ are introduced by generalizing (2.47):

$$\vec{u}(\kappa^\ell) = (Nm_\kappa)^{-\frac{1}{2}} \sum_{\vec{q}_j} \vec{e}(\kappa | \vec{q}_j) \exp[i\vec{qr}(\kappa^\ell)] Q(\vec{q}_j) . \quad (3.53)$$

The relations analogous to (2.48,49) are

$$Q(-\vec{q}_j) = Q^*(\vec{q}_j) , \quad (3.54)$$

$$Q(\vec{q}_j) = \frac{1}{2} [A(\vec{q}_j) e^{-i\omega_j(\vec{q})t} + A^*(-\vec{q}_j) e^{i\omega_j(\vec{q})t}] . \quad (3.55)$$

In Appendix I it is shown that in terms of normal coordinates, the Hamiltonian (3.14) assumes the form (2.58)

$$H = \frac{1}{2} \sum_{\vec{q}_j} \left[P^*(\vec{q}_j) P(\vec{q}_j) + \omega_j^2(\vec{q}) Q^*(\vec{q}_j) Q(\vec{q}_j) \right] , \quad (3.56)$$

where

$$P(\vec{q}_j) = \dot{Q}(\vec{q}_j) . \quad (3.57)$$

Furthermore, the normal coordinates satisfy the uncoupled harmonic oscillator equation

$$\ddot{Q}(\vec{q}_j) + \omega_j^2(\vec{q}) Q(\vec{q}_j) = 0 . \quad (3.58)$$

The equations analogous to (2.53,56) are

$$Q(\vec{q}_j) = N^{-\frac{1}{2}} \sum_{\ell\kappa} m_\kappa^{\frac{1}{2}} \exp[-i\vec{qr}(\kappa^\ell)] \vec{e}^*(\kappa | \vec{q}_j) \vec{u}(\kappa^\ell) , \quad (3.59)$$

$$P(\vec{q}_j) = N^{-\frac{1}{2}} \sum_{\ell\kappa} m_\kappa^{-\frac{1}{2}} \exp[-i\vec{qr}(\kappa^\ell)] \vec{e}^*(\kappa | \vec{q}_j) \vec{p}(\kappa^\ell) . \quad (3.60)$$

As in the case of the diatomic chain, it is possible to introduce *real normal coordinates* $\alpha_v(\vec{q}_j)$ (standing waves) or $\eta(\vec{q}_j)$ (running waves). They are defined by expressions analogous to (2.62,67), respectively.

The classical mean energy of the system is given by the relations (2.73,74)

$$\bar{E} = \frac{1}{2} \sum_{\vec{q}_j} \omega_j^2(\vec{q}) |A(\vec{q}_j)|^2 = \sum_{\vec{q}_j} \bar{E}_j(\vec{q}) , \quad (3.61)$$

where

$$\bar{E}_j(\vec{q}) = \frac{1}{2} \omega_j^2(\vec{q}) |A(\vec{q}_j)|^2 = k_B T . \quad (3.62)$$

If there are n atoms in the primitive unit cell, the index j runs from $1 \dots 3n$; for a crystal with N primitive unit cells, the wave vector \vec{q} assumes N distinct values as is evident from (3.40a,b). From (3.61,62), we therefore obtain for the total mean energy

$$\bar{E} = 3nNk_B T . \quad (3.63)$$

The classical specific heat is therefore given by (Dulong and Petit)

$$c_V = \frac{d\bar{E}}{dT} = 3nNk_B . \quad (3.64a)$$

Thus, each of the nN atoms of the crystal contributes $3 k_B$ to the specific heat. If the crystal contains one mole of molecules (or formula units) with s atoms per molecule, we have sN_L atoms, where N_L is Loschmidt's number. Introducing the gas constant $R = N_L k_B$, the molar specific heat is therefore given by

$$C_V = 3sR . \quad (3.64b)$$

The commutator relations corresponding to (2.111) are

$$\begin{aligned} [u_\alpha(\ell), p_\beta(\ell')] &= i\hbar\delta_{\ell\ell'}\delta_{\kappa\kappa'}\delta_{\alpha\beta} \\ [u_\alpha(\ell), u_\beta(\ell')] &= [p_\alpha(\ell), p_\beta(\ell')] = 0 . \end{aligned} \quad (3.65)$$

Using (3.29, 59, 60, 65) and the lattice sum (2.51) generalized to the three-dimensional case, namely,

$$\sum_\ell e^{i(\vec{q}-\vec{q}')\vec{r}(\ell)} = N\Delta(\vec{q} - \vec{q}') , \quad (3.66)$$

we obtain the commutator relations analogous to (2.112)

$$[Q^*(\vec{q}), P(\vec{q}', j)] = i\hbar\Delta(\vec{q} - \vec{q}')\delta_{jj'} , \quad (3.67a)$$

$$[Q(\vec{q}, j), P^*(\vec{q}', j')] = i\hbar\Delta(\vec{q} - \vec{q}')\delta_{jj'} , \quad (3.67b)$$

$$[Q^*(\vec{q}, j), Q(\vec{q}', j')] = [P^*(\vec{q}, j), P(\vec{q}', j')] = 0 . \quad (3.67c)$$

According to (2.113,114), we define *creation and annihilation operators* by means of the relations

$$Q(\vec{q}, j) = \left(\frac{\hbar}{2\omega_j(\vec{q})} \right)^{\frac{1}{2}} [a^+(-\vec{q}, j) + a(\vec{q}, j)] , \quad (3.68)$$

$$P(\vec{q}_j) = i \left(\frac{\hbar \omega_j(\vec{q})}{2} \right)^{\frac{1}{2}} [a^+(\vec{-q}_j) - a(\vec{q}_j)] . \quad (3.69)$$

According to (2.117), these operators satisfy the commutator relations

$$\begin{aligned} [a(\vec{q}_j), a^+(\vec{q}'_j)] &= \Delta(\vec{q} - \vec{q}') \delta_{jj'} \\ [a(\vec{q}_j), a(\vec{q}'_j)] &= [a^+(\vec{q}_j), a^+(\vec{q}'_j)] = 0 \end{aligned} \quad (3.70)$$

and as in (2.119), the Hamilton operator assumes the form

$$H = \sum_{\vec{q}j} \hbar \omega_j(\vec{q}) [a^+(\vec{q}_j) a(\vec{q}_j) + \frac{1}{2}] . \quad (3.71)$$

The equations corresponding to (2.122,123) are

$$a_s^+ |...n_s...> = (n_s + 1)^{\frac{1}{2}} |...n_s + 1...> , \quad (3.72)$$

$$a_s |...n_s...> = n_s^{\frac{1}{2}} |...n_s - 1...> , \quad (3.73)$$

where s stands for $(\vec{q}j)$ and $|...n_s...>$ are eigenfunctions of H .

The individual matrix elements of a_s^+ and a_s are given by (2.124,125). For further reference, we express the displacements $\vec{u}_{(k)}^{(\ell)}$ and the momenta $\vec{p}_{(k)}^{(\ell)} = m_k \vec{u}_{(k)}^{(\ell)}$ in terms of creation and annihilation operators. From (3.53, 68), we obtain

$$\vec{u}_{(k)}^{(\ell)} = \left(\frac{\hbar}{2Nm_k} \right)^{\frac{1}{2}} \sum_{\vec{q}j} [\omega_j(\vec{q})]^{-\frac{1}{2}} e_{(k)}(\vec{q}_j) \exp[i\vec{q}\vec{r}_{(k)}^{(\ell)}] [a^+(\vec{-q}_j) + a(\vec{q}_j)] \quad (3.74)$$

and using (3.53,57,69) gives

$$\vec{p}_{(k)}^{(\ell)} = i \left(\frac{\hbar m_k}{2N} \right)^{\frac{1}{2}} \sum_{\vec{q}j} [\omega_j(\vec{q})]^{\frac{1}{2}} e_{(k)}(\vec{q}_j) \exp[i\vec{q}\vec{r}_{(k)}^{(\ell)}] [a^+(\vec{-q}_j) - a(\vec{q}_j)] . \quad (3.75)$$

3.5 Density of States and Specific Heat

3.5.1 Density of States

One frequently encounters lattice properties that are sums of the form

$$S = \sum_{\vec{q}j} K[\omega_j(\vec{q})] . \quad (3.76)$$

Examples are the mean energy \bar{E} given by (2.131) or the specific heat $c_V = d\bar{E}/dT$. Since the density of the values of \vec{q} in reciprocal space is high and is given by $\Gamma(\vec{q}) = V/(2\pi)^3$, (3.44), we can write

$$S = \frac{V}{(2\pi)^3} \sum_j \int_{BZ} K(\omega_j(\vec{q})) d^3 q , \quad (3.77)$$

where the integration extends over the first Brillouin zone (BZ). Equation (2.133a) is an example of such an expression for the mean energy of the diatomic chain. On the other hand, if we regard K as a function of ω and introduce the density of normal modes

$$g(\omega) = \sum_j g_j(\omega) \quad (3.78)$$

such that $g(\omega)d\omega$ is the total number of modes with frequencies between ω and $\omega + d\omega$, see (2.138), the expression (3.76) can be written in the form

$$S = \int K(\omega)g(\omega)d\omega . \quad (3.79)$$

An example of such a frequency integral is the specific heat given by (2.142). By comparing (3.79) with (3.77), we obtain

$$g(\omega) = \frac{V}{(2\pi)^3} \sum_j \int_{BZ} \delta[\omega - \omega_j(\vec{q})] d^3 q . \quad (3.80)$$

In fact, if we substitute (3.80) in (3.79) and use the relation

$$\int d\omega \delta[\omega - \omega_j(\vec{q})] K(\omega) = K[\omega_j(\vec{q})] ,$$

we obtain (3.77). The normalizing condition for $g(\omega)$ is clearly given by

$$\int g(\omega) d\omega = 3nN , \quad (3.81)$$

where n is the number of atoms per unit cell and N is the number of unit cells.

Since $\lambda = \omega^2$ appears as the eigenvalue of the dynamical matrix, see (3.25), it is sometimes useful to define a function $G(\omega^2)$ such that $G(\omega^2)d\omega^2$ is the fraction of allowed eigenvalues in the region ω^2 to $\omega^2 + d\omega^2$. Since $G(\omega^2)d\omega^2 = g(\omega)d\omega$ and $d\omega^2 = 2\omega d\omega$, the relation between the two functions is

$$G(\omega^2) = \frac{1}{2\omega} g(\omega) . \quad (3.82)$$

We now derive an alternative expression for $g(\omega)$ which is useful for practical calculations and also reflects the singularities in $g(\omega)$. Since $g_j(\omega)d\omega$ is the number of modes (\vec{q}_j) in the frequency interval $\omega_j = \omega$ to $\omega_j + d\omega_j$, we can write

$$g_j(\omega) d\omega = \int_{\text{shell}} r(\vec{q}) d\vec{q} = \frac{V}{(2\pi)^3} \int_{\text{shell}} d^3 q , \quad (3.83a)$$

where the integration extends over the volume $d^3 q$ from a surface of constant frequency $\omega_j = \omega$ to another at $\omega_j + d\omega_j$ (Fig. 3.8a). Figure 3.8b shows that the volume element $d^3 q$ between the constant frequency surfaces ω_j and $\omega_j + d\omega_j$ is a cylinder of base dS_{ω_j} and height dq_{\perp} . Hence

$$g_j(\omega) d\omega = \frac{V}{(2\pi)^3} \int dS_{\omega_j} dq_{\perp} . \quad (3.83b)$$

From Fig. 3.8b it follows that

$$\begin{aligned} d\omega_j &= d\omega = \nabla \omega_j(\vec{q}) d\vec{q} \\ &= |\nabla \omega_j(\vec{q})| |d\vec{q}| \cos \alpha = |\nabla \omega_j(\vec{q})| dq_{\perp} , \end{aligned}$$

where $\nabla \omega_j(\vec{q})$ is the q gradient of $\omega_j(\vec{q})$. Substituting dq_{\perp} from this expression in (3.83b) and dividing both sides by $d\omega$, we obtain the result

$$g_j(\omega) = \frac{V}{(2\pi)^3} \int_{\omega_j=\omega} \frac{dS_{\omega_j}}{v_{gj}(\omega_j)} , \quad (3.84)$$

where

$$\vec{v}_{gj}(\omega_j) = \nabla \omega_j(\vec{q}) \quad (3.85)$$

is the *group velocity* of the mode (\vec{q}, j) . In (3.84), the integral is over that surface in the first Brillouin zone on which $\omega_j(\vec{q}) = \omega$. Substituting (3.84) in (3.78), we obtain

$$g(\omega) = \frac{V}{(2\pi)^3} \sum_j \int_{\omega_j=\omega} \frac{dS_{\omega_j}}{v_{gj}(\omega_j)} . \quad (3.86)$$

The analogous expressions for the one-dimensional chain are given by (2.139, 140).

For the diatomic linear chain, we have shown that there are singularities in $g(\omega)$ at certain critical points (c.p.) where the group velocity vanishes (Fig. 2.11a). Critical points also exist in two and three-dimensional lattices. The character of these singularities can be discussed by expanding the frequency in a Taylor's series about the frequency ω_c of the c.p. If $\vec{v}_{gj} = 0$, then according to (3.85), the linear terms in the Taylor's series are absent and the variation in the frequency is approximately given by

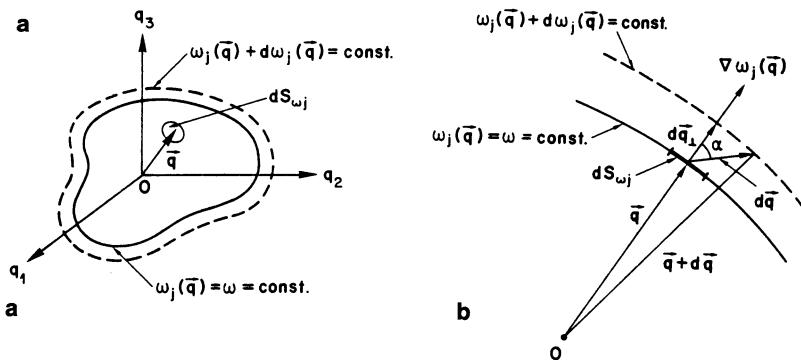


Fig. 3.8. a) Surfaces of constant Frequencies in \vec{q} space. b) Two neighbouring surfaces of constant frequencies illustrating the calculation of $g_j(\omega)$

$$\omega(\vec{q}) = \omega_c + \sum_{i=1}^3 c_i (q_i - q_{ci})^2 . \quad (3.87)$$

Here, q_i is the component of \vec{q} along one of the *principal directions* of the BZ and \vec{q}_c is the wave vector at the c.p. The character of the singularity of $g_j(\omega)$ at the c.p. is obtained by substituting (3.87) in (3.84). $g_j(\omega)$ behaves differently near the c.p. depending on whether the c.p. is a maximum [all $c_i < 0$ in (3.87)], a minimum (all $c_i > 0$) or a saddle point (two of the c_i are positive and one is negative, or vice versa). In contrast to the one-dimensional lattice, $g_j(\omega)$ itself does not show any infinities or discontinuities in three dimensions; for a three-dimensional lattice, only the derivative $dg_j(\omega)/d\omega$ is discontinuous. It can be shown that $g_j(\omega)$ is of the form (Problem 3.8.1)

$$g_j(\omega) \sim \begin{cases} (\omega_c - \omega)^{\frac{1}{2}} & \text{for } \omega < \omega_c \\ 0 & \text{for } \omega > \omega_c \end{cases} \quad (3.88)$$

in the case of a maximum and vice versa in the case of a minimum. The behaviour at saddle points is not essentially different. Other branches may also contribute to $g(\omega) = \sum_j g_j(\omega)$, but not discontinuously, so that the structure due to the c.p. can occur on a continuous background. In the case of a maximum, $g(\omega)$ falls parabolically as $\omega \rightarrow \omega_c$, at which point it discontinuously changes slope. Thus, these singularities are of a rather harmless type and do not complicate the numerical computations. These critical points were first discussed by VAN HOVE [3.7]. PHILLIPS [3.8] has extended VAN HOVE's analysis. More elementary discussions have been given by WANNIER

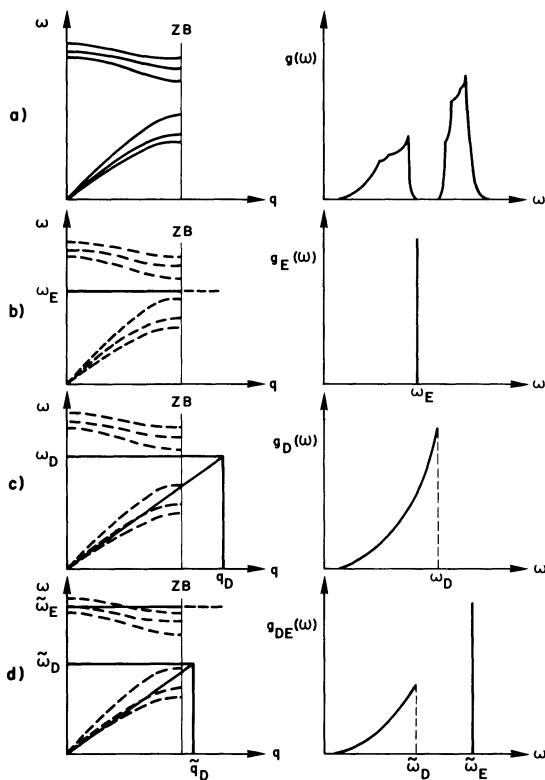


Fig.3.9. Phonon dispersion and density of state for a crystal with two atoms in the primitive unit cell. a) Qualitative general behaviour, b) Einstein approximation, c) Debye approximation, and d) Hybride Einstein-Debye model. The corresponding situation for the diatomic linear chain is shown in Fig. 2.11

[3.9] and DECIUS and HEXTER [3.10]. From (3.85,86), it is possible to calculate the density of states if the dispersion $\omega_j(\vec{q})$ is known. The qualitative behaviour of $g(\omega)$ for a diatomic three-dimensional crystal is shown in Fig.3.9a. An example of such a density of states derived from observed and calculated phonon dispersions will be discussed below. However, we first consider the simpler Einstein and Debye approximations just as we have done for the diatomic linear chain (Sect.2.2.5).

The most drastic simplification is the *Einstein model* which postulates that the atoms of a solid oscillate independently with the same frequency ω_E , the *Einstein frequency*. Since ω_E is independent of q , the dispersion relation for this model can be represented by a horizontal line and the corresponding density of states is a δ -function centered at $\omega = \omega_E$ (Fig.3.9b).

For a crystal with N unit cells and n atoms per unit cell, the Einstein density of states is

$$g_E(\omega) = 3nN\delta(\omega - \omega_E) . \quad (3.89)$$

$g_E(\omega)$ obviously satisfies the normalizing condition (3.81). The frequency ω_E is chosen such that the best agreement is obtained between experimental and theoretical specific heat and other derived properties.

Next we consider the *Debye model* which replaces all branches (acoustical and optical) by three branches, each of which with the same linear dispersion

$$\omega = v q , \quad (3.90)$$

where v is a *mean sound velocity* for the three acoustic branches which is independent of q . As we have pointed out for the diatomic chain, the optic branches are represented by the high q values of the same linear expression (3.90) whose low q values give the acoustic branches (Fig.3.9c). Since $\omega^2 = v^2 q^2 = v^2 (q_1^2 + q_2^2 + q_3^2)$, the surface of constant frequency is a sphere of radius q , the *Debye sphere*. Since $v_{gj} = v$ and $\int dS_\omega = 4\pi q^2$, we obtain from (3.86) by summing over the three acoustic branches for the Debye density of states

$$g_D(\omega) = \frac{3}{2\pi^2} V \frac{\omega^2}{v^3} , \quad (3.91)$$

where $V = Nv_a$ is the volume of the crystal. Using the normalizing condition

$$\int_0^{\omega_D} g_D(\omega) d\omega = 3nN , \quad (3.92)$$

where n is the number of atoms in the primitive unit cell and ω_D is the *Debye frequency*, we obtain from (3.91,92)

$$\omega_D^3 = \frac{n}{V_a} 6\pi^2 v^3 . \quad (3.93)$$

Substituting (3.93) in (3.91) gives (Fig.3.9c)

$$g_D(\omega) = \begin{cases} 9nN \frac{\omega^2}{\omega_D^3} & \text{for } \omega < \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} . \quad (3.94)$$

The radius of the Debye sphere is given by $q_D = \omega_D/v$ and from (3.93) we obtain

$$q_D = \left(6\pi^2 \frac{n}{V_a} \right)^{1/3} . \quad (3.95)$$

As we have seen in Sect.2.2.5, the Einstein model represents the optical modes well, especially if their dispersion is weak, while the Debye model is more adapted to the acoustical modes. For this reason, the Debye model is often applied only to the acoustic modes and the Einstein model only to the optic modes. The corresponding approximations for the dispersion relation are shown in Fig.3.9d. For the density of states, we write in this case

$$\tilde{g}_{DE}(\omega) = \tilde{g}_D(\omega) + \tilde{g}_E(\omega) . \quad (3.96)$$

$\tilde{g}_E(\omega)$ is the Einstein density of states which represents the 3n-3 optical branches and is given by

$$\tilde{g}_E(\omega) = (3n - 3)N\delta(\omega - \tilde{\omega}_E) , \quad (3.97)$$

where $\tilde{\omega}_E$ is a mean optical frequency. The Debye density of states, $\tilde{g}_D(\omega)$, is given by (3.91) but the normalizing condition is now

$$\int_0^{\tilde{\omega}_D} \tilde{g}_D(\omega) d\omega = 3N , \quad (3.98)$$

from which it follows that

$$\tilde{\omega}_D^3 = \frac{1}{V_a} 6\pi^2 V^3 = \frac{1}{n} \omega_D^3 \quad (3.99)$$

and

$$\tilde{g}_D(\omega) = \begin{cases} 9N \omega^2 / \tilde{\omega}_D^3 & \text{for } \omega < \tilde{\omega}_D \\ 0 & \text{for } \omega > \tilde{\omega}_D . \end{cases} \quad (3.100)$$

The radius of the Debye sphere is now

$$\tilde{q}_D = \left(\frac{6\pi^2}{V_a} \right)^{1/3} = n^{-1/3} q_D . \quad (3.101)$$

$\tilde{g}_E(\omega)$ and $\tilde{g}_D(\omega)$ are shown in Fig.3.9d. For the monoatomic crystal with only one atom per unit cell ($n = 1$), $\tilde{g}_E(\omega) = 0$ and $\tilde{\omega}_D = \omega_D$, $\tilde{g}_D(\omega) = g_D(\omega)$.

3.5.2 Specific Heat

In Sect.2.2.5, we obtained for the specific heat (2.142)

$$c_V(T) = k_B \int \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp(\hbar\omega/k_B T) g(\omega)}{[\exp(\hbar\omega/k_B T) - 1]^2} d\omega . \quad (3.102)$$

Substituting (3.89) in (3.102) and introducing the *Einstein temperature* θ_E by

$$k_B \theta_E = \hbar \omega_E , \quad (3.103)$$

we obtain for the *Einstein specific heat*

$$c_E(T) = 3nNk_B \left(\frac{\theta_E}{T} \right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2} . \quad (3.104)$$

At high temperatures ($T \gg \theta_E$) we obtain the classical value (3.64a), namely, $c_E(T) = 3nNk_B$, while at low temperatures ($T \ll \theta_E$) the Einstein approximation gives

$$c_E(T) = 3nNk_B \left(\frac{\theta_E}{T} \right)^2 \exp(-\theta_E/T) \quad (T \ll \theta_E) . \quad (3.105)$$

The Einstein specific heat is shown in Fig.3.10.

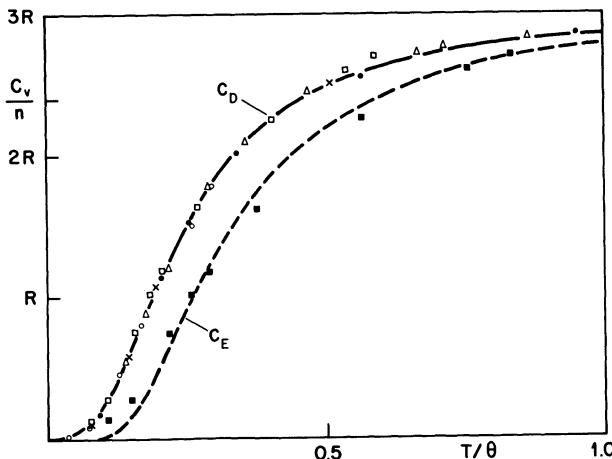


Fig.3.10. Einstein and Debye specific heat as a function of reduced temperature. θ is either the Einstein or the Debye temperature, depending on which curve is being examined. The Debye specific heat is compared with the observed specific heats of Ag(\bullet), $\theta_D = 215$ K; Al(Δ), $\theta_D = 394$ K; C(diamond)(\square), $\theta_D = 1860$ K; Al_2O_3 (\circ), $\theta_D = 937$ K; KCl(x), $\theta_D = 227$ K; and the Einstein specific heat with C(diamond) (\blacksquare) $\theta_E = 1320$ K, [3.11,12]

Substituting (3.94) in (3.102) and defining the *Debye temperature* θ_D by

$$k_B \theta_D = \hbar \omega_D , \quad (3.106)$$

we obtain for the *Debye specific heat*

$$c_D(T) = 9nNk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx , \quad (3.107)$$

where we have used the abbreviation $x = \hbar\omega/k_B T$. If $T \gg \Theta_D$, we again obtain the classical result $c_D = 3nNk_B$ as can be seen by developing the integrand for small values of x . If $T \rightarrow 0$, the integral in (3.107) may be extended to infinity, in which case it has the value $12\pi^4/45$. We obtain, therefore, the famous T^3 law for the specific heat of a three-dimensional crystal

$$c_D(T) = \frac{12\pi^4}{5} nNk_B \left(\frac{T}{\Theta_D}\right)^3 \quad (T \ll \Theta_D) . \quad (3.108)$$

It is interesting to compare this result with the corresponding result for the linear chain (2.161) where $c_D \sim T$. It can be shown that for a two-dimensional lattice, $c_D \sim T^2$ (Problem 3.8.3). The Debye specific heat is shown in Fig.3.10. This figure shows that at low temperatures, the Einstein specific heat is much smaller than the Debye specific heat, reflecting the difficulty in thermally exciting optical modes at low temperatures. In Fig.3.10, the Debye specific heat is also compared with specific heat data of several simple substances. The agreement between theory (3.107) and experiment is surprisingly good and considerably better than for the Einstein approximation, especially at low temperatures. Table 3.1 contains Debye temperatures of a number of selected substances.

The Debye theory is so firmly established that it has become common practice to express specific heat data in terms of an "equivalent Debye temperature". For an experimental measurement or for a calculated value of $c_V(T)$ via (3.102), we can define an equivalent Debye temperature; this is the value of Θ_D that must be used in (3.107) such that $c_D(T/\Theta_D) = c_V(T)$. Unless the crystal is exactly described by the Debye model (which will never be the case), the equivalent Debye temperature depends on T , since no single value of Θ_D will satisfy $c_D(T) = c_V(T)$ at all temperatures. Thus, the experimental or theoretical specific heat data are usually presented as a plot of Θ_D against T and in this way, show the deviations of the crystal from a Debye solid. An example of $\Theta_D(T)$ is shown in Fig.3.11 for potassium. Most materials yield a curve of $\Theta_D(T)$ of the same general form. The T^3 law, which depends on the constancy of Θ_D , can be accurate over a rather small temperature range only, up to about $(1/50)\Theta_D$, but Fig.3.11 shows that Θ_D is still a useful parameter even if it has lost its accuracy.

Table 3.1. Debye temperatures θ_D for selected substances [3.11,13] (mean values)

Substance	θ_D [K]	Substance	θ_D [K]	Substance	θ_D [K]
Li	400	La	132	Pb	88
Na	150	Ni	375	As	285
K	100	Pd	275	Sb	200
Rb	55	Pt	230	Bi	120
Cs	39				
Be	1000	Cu	315	Ne	63
Mg	318	Ag	215	Ar	85
Ca	230	Au	170	Kr	63
		Zn	234	Xe	55
Ti	380	Cd	120	NaCl	281
Zr	280	Hg	100	NaI	170
Hf	213			KBr	150
		B	1250	KI	140
Cr	460	Al	394	RbF	240
Mo	380	Ga	240	RbI	110
W	310	In	129	AgF	269
		Tl	96	AgCl	163
Fe	420	C ^a	1860	AgBr	121
Os	250			CuCl	187
		Si	625		
Co	385	Ge	360	CaF ₂	474
Ir	285			FeS ₂	645

^aDiamond

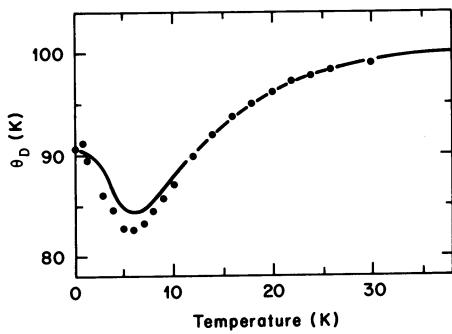


Fig. 3.11. The Debye temperature $\theta_D(T)$ for potassium. The points represent the results obtained from measured values of the specific heat; the full line is obtained from $c_D[T/\theta_D(T)] = c_V(T)$, where $c_V(T)$ is given by (3.102) with $g(\omega)$ calculated on the basis of a theoretical model [3.14]

From the discussion given above, it is clear that the Debye temperature is a measure of the temperature separating the low temperature regime where quantum statistics must be used from the high temperature region where classical statistics applies. In other words, θ_D is a measure of the temperature

above which all modes begin to be excited, and below which modes begin to be "frozen out". The Debye temperature also reflects the strength of interatomic forces: from Table 3.1 it is seen that $\theta_D \approx 2000$ K for diamond with strong covalent bonds between the carbon atoms, but only 63 K for solid Ne with very weak Van der Waals bonds acting between the Ne atoms. In the latter case, the melting point of 25.4 K is well below the Debye temperature.

We now derive the expression for the specific heat which is based on the hybrid density of states (3.96). Substituting (3.96,97,100) in (3.102) and defining Debye and Einstein temperatures by $k_B\tilde{\theta}_D = \hbar\omega_D$, $k_B\tilde{\theta}_E = \hbar\omega_E$, respectively, we obtain

$$c_{DE}(T) = 9Nk_B \left(\frac{T}{\tilde{\theta}_D}\right)^3 \int_0^{\tilde{\theta}_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + (3n - 3)Nk_B \left(\frac{\tilde{\theta}_E}{T}\right)^2 \frac{\exp(\tilde{\theta}_E/T)}{[\exp(\tilde{\theta}_E/T) - 1]^2} . \quad (3.109)$$

At high temperatures, (3.109) again gives the classical result $3nNk_B$. At sufficiently low temperatures, the Einstein term in (3.109) can be neglected with the result that

$$c_{DE}(T) = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\tilde{\theta}_D}\right)^3 \quad (\text{for } T \ll \tilde{\theta}_D) . \quad (3.110)$$

According to the definitions of θ_D and $\tilde{\theta}_D$ and the relation (3.99), it follows that $\tilde{\theta}_D^3 = \theta_D^3/n$, and therefore the coefficient of T^3 in (3.110) is exactly the same as in (3.108). The specific heat (3.109) depends on the two parameters $\tilde{\theta}_D$ and $\tilde{\theta}_E$ which allow more flexibility in adjusting experimental data. Of course, it is also possible to introduce several Einstein temperatures $\tilde{\theta}_{Ej}$ corresponding to the different optical branches. This might be necessary if we are dealing with a molecular crystal such as benzene with a large number of intramolecular optical modes (Chap.4), the frequencies of which are widely different.

We will now discuss the density of states and the specific heat of β -AgI as derived from observed and calculated phonon dispersions [3.15]. The hexagonal unit cell and the crystal structure of β -AgI are shown in Fig.3.7a; Fig.3.7b illustrates the corresponding Brillouin zone. The observed and calculated phonon dispersions are depicted in Fig.3.12. β -AgI contains 4 ions in the unit cell which gives rise to 12 branches. A valence-shell model (Chap.4) has been used to calculate $\omega_j(\vec{q})$ and the parameters of this model have been adjusted such that good agreement is obtained with the observed

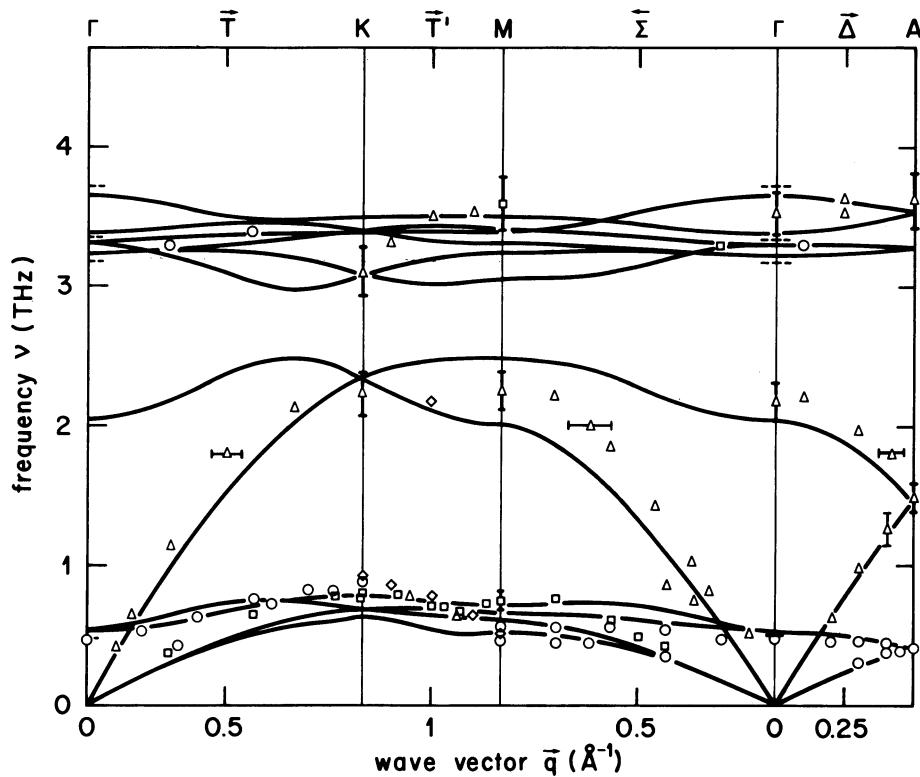


Fig. 3.12. Observed and calculated phonon dispersion of β -AgI. Solid lines: valence-shell model [3.15]

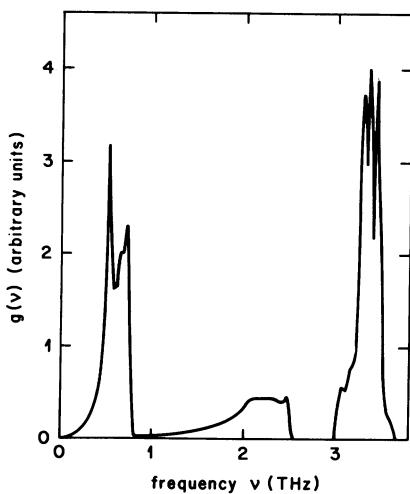


Fig. 3.13. Frequency distribution $g(\nu)$ of phonons in β -AgI calculated on the basis of the valence-shell model [3.15]

phonon dispersion. The density of states has then been calculated on the basis of (3.86) using a digital computer and the result is shown in Fig.3.13. The flat dispersion of the optic and transverse-acoustic modes gives rise to two sharp maximum separated by the broad distribution of the LA modes and a small frequency gap. It should be pointed out that such a low-lying and flat optic branch as observed in β -AgI near 0.5 THz (Fig.3.12), is quite unusual and contributes to the low-frequency peak in $g(\omega)$ of Fig.3.13. Based on the density of states, the specific heat has been calculated numerically using the expression (3.102). The result is shown in Fig.3.14. Comparison is made with experimental values. Corrections $c_p \rightarrow c_V$ (Chap.5) can be neglected for temperatures below 100 K. The quasilinear behaviour of c_V between 15 and 50 K is well reproduced by the calculation. This peculiar shape is a consequence of the "non-Debye" density of states $g(\omega)$. This is also reflected in $\Theta_D(T)$ of β -AgI [3.15] which shows a much stronger variation than in the case of potassium (Fig.3.11). At higher temperatures, c_p has contributions from defect creation and anharmonicity (Chap.5) and exceeds the computed c_V values.

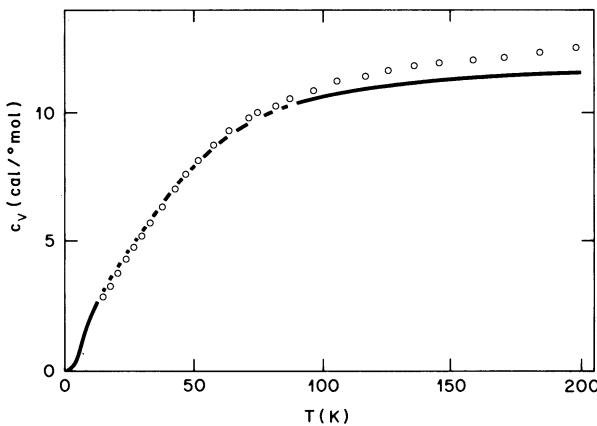


Fig.3.14. Specific heat $c_V(T)$ for β -AgI. Solid line: derived from $g(\nu)$ shown in Fig.3.13 and using (3.102) [3.15]; experimental points from [3.16]

3.6 Connection of Lattice Dynamics with the Theory of Elasticity

In Appendix H we demonstrate that for the case of the so-called acoustic modes in the limit of infinitely long waves, the atoms in a unit cell move in parallel having vanishing frequency. For very small values of \vec{q} , this result is still approximately true and the corresponding three frequencies

for a given wave vector \vec{q} are small. These low frequency vibrations correspond to *sound waves*, the frequencies of which are determined by the macroscopic elastic constants and the density of the crystal. On the other hand, the frequencies of all the modes are determined by the atomic force constants $\phi_{\alpha\beta}^{(\ell\ell')}(k\kappa')$ and the masses of the atoms. Therefore, relations between the elastic constants and the atomic force constants must exist. In order to avoid lengthy calculations, we shall discuss these relations for the case of crystals with only one atom per unit cell.

For a Bravais lattice we can drop the indices k and k' in (3.15) and obtain for the force which acts on the atom in unit cell 0

$$m\ddot{u}_\alpha(0) = - \sum_{\ell\beta} \phi_{\alpha\beta}(0\ell) u_\beta(\ell) . \quad (3.111)$$

Since the wavelengths of sound waves are very large compared with the lattice constant, the variation of the displacements $\vec{u}(\ell)$ are very slight from cell to cell. We therefore define a spatially slowly-changing displacement field $\vec{u}(\vec{x})$ which is equal to $\vec{u}(\ell)$ at the lattice sites $\vec{r}(\ell)$ (Fig. 3.15)

$$\vec{u}[\vec{x} = \vec{r}(\ell)] = \vec{u}(\ell) . \quad (3.112)$$

Expanding the field \vec{u} at the site $\vec{r}(\ell) = \vec{r}_\ell$ about the origin at $\vec{r}(0) = 0$, we obtain

$$u_\beta(\ell) = u_\beta(0) + \sum_\gamma u_\beta|_\gamma r_{\ell\gamma} + \frac{1}{2} \sum_{\gamma\lambda} u_\beta|_{\gamma\lambda} r_{\ell\gamma} r_{\ell\lambda} , \quad (3.113)$$

where $r_{\ell\gamma}$ is the component of $r(\ell)$ in the direction γ and

$$u_\beta|_\gamma = \left(\frac{\partial u_\beta}{\partial x_\gamma} \right)_0 , \quad u_\beta|_{\gamma\lambda} = \left(\frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\lambda} \right)_0 \quad (3.114)$$

and the subscript zero means that the derivatives are evaluated at the origin $\vec{x} = 0$.

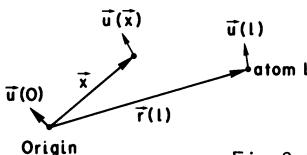


Fig. 3.15. Spatially slowly changing displacement field $\vec{u}(\vec{x})$ describing the long-wavelength acoustic vibrations

Substituting (3.113) in (3.111), the first term disappears because of (3.17a) and the second because of (3.19) and introducing the density $\rho = m/v_a$, we obtain

$$\rho \ddot{u}_\alpha(\ell) = \rho \ddot{u}_\alpha = \sum_{\beta\gamma\lambda} \tilde{C}_{\alpha\beta,\gamma\lambda} u_\beta |_{\gamma\lambda} . \quad (3.115)$$

Here the coefficients $\tilde{C}_{\alpha\beta,\gamma\lambda}$ are given by

$$\tilde{C}_{\alpha\beta,\gamma\lambda} = - \frac{1}{2v_a} \sum_\ell \Phi_{\alpha\beta}(0\ell) r_{\ell\gamma} r_{\ell\lambda} . \quad (3.116)$$

By using the expansion (3.113), we have tacitly assumed that contributions to the sum in (3.111) only come from regions where \vec{u} does not change much. This will be satisfied trivially if the force constants $\Phi_{\alpha\beta}(0\ell)$ can be neglected for distances r larger than some r_0 .

From the definition (3.116) and from (3.16), it follows that

$$\tilde{C}_{\alpha\beta,\gamma\lambda} = \tilde{C}_{\beta\alpha,\gamma\lambda} = \tilde{C}_{\alpha\beta,\lambda\gamma} . \quad (3.117)$$

Furthermore, HUANG has shown that if the crystal is initially free of stresses, the quantity $\tilde{C}_{\alpha\beta,\gamma\lambda}$ is invariant under the transposition $\alpha\beta \leftrightarrow \gamma\lambda$, that is [3.17]

$$\tilde{C}_{\alpha\beta,\gamma\lambda} = \tilde{C}_{\gamma\lambda,\alpha\beta} . \quad (3.118)$$

It can be shown that the HUANG conditions (3.118) follow directly from the transformation properties of the force on an atom under a rigid body rotation of the crystal [3.18]. As a result of (3.117,118), the number of independent components of $\tilde{C}_{\alpha\beta,\gamma\lambda}$ is reduced to 21.

We now regard the crystal as an elastic continuum. Excellent treatments of the theory of elasticity have been given in several texts [3.1,19-21]. In the following we summarize the most important results. A body which is acted on by external forces, or, more generally, a body on which one part exerts a force on neighbouring parts, is said to be in a state of stress. Consider a unit cell within the body (Fig.3.16) with edges parallel to the unit vectors $\vec{f}_1, \vec{f}_2, \vec{f}_3$. A force will be transmitted across each face of the cube, exerted by the material outside the cube upon the material inside the cube. The force transmitted across each face may be resolved into three components parallel to $\vec{f}_1, \vec{f}_2, \vec{f}_3$. We denote by $\sigma_{\alpha\beta}$ the component of the force in the \vec{f}_α -direction transmitted across that face of the cube which is perpendicular to \vec{f}_β . For the unit cube to be in translational and rotational equilibrium there can be only six independent components of stress which means that the stress tensor σ is symmetrical:

$$\sigma_{\alpha\beta} = \sigma_{\beta\alpha} . \quad (3.119)$$

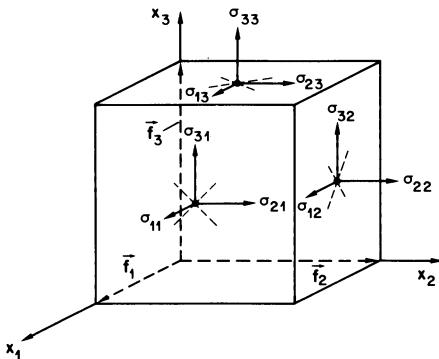


Fig. 3.16. The forces on the faces of a unit cube in a stressed body. σ_{23} is the component of the force in the \vec{f}_2 -direction transmitted across the face of the cube which is perpendicular to \vec{f}_3

The diagonal elements σ_{11} , σ_{22} , σ_{33} are the *normal components* of stress while σ_{12} , σ_{13} , and σ_{23} are the *shear components*.

The stresses will cause deformations in the solid which are described by a *symmetrical deformation tensor* ϵ defined by

$$\epsilon_{\gamma\lambda} = \epsilon_{\lambda\gamma} = \frac{1}{2} (u_\gamma|_\lambda + u_\lambda|\gamma) , \quad (3.120)$$

where the *strain components* $e_{\gamma\lambda} = u_\gamma|_\lambda$ are defined by (3.114). e_{11} , e_{22} , e_{33} are the extensions per unit length parallel to \vec{f}_1 , \vec{f}_2 , \vec{f}_3 , respectively, while $e_{\alpha\beta}$ ($\alpha \neq \beta$) are related to the changes in angle between the axis \vec{f}_α and \vec{f}_β before and after the deformation [3.19].

What is the relation between stress and deformation? *Hooke's law* states that for sufficiently small deformations, the deformation is directly proportional to the stress, that is,

$$\epsilon_{\alpha\beta} = \sum_{\gamma\lambda} S_{\alpha\beta,\gamma\lambda} \sigma_{\gamma\lambda} . \quad (3.121)$$

The quantities $S_{\alpha\beta,\gamma\lambda}$ are the *elastic compliance constants* of the crystal. Conversely, the stress components are linear functions of the deformation components

$$\sigma_{\alpha\beta} = \sum_{\gamma\lambda} C_{\alpha\beta,\gamma\lambda} \epsilon_{\gamma\lambda} . \quad (3.122)$$

The quantities $C_{\alpha\beta,\gamma\lambda}$ are the *elastic stiffness constants* or simply the *elastic constants*. The elastic energy density (normalized to the volume of the unstrained crystal) is given by

$$w = \frac{1}{2} \sum_{\alpha\beta} \sum_{\gamma\lambda} C_{\alpha\beta,\gamma\lambda} \epsilon_{\alpha\beta} \epsilon_{\gamma\lambda} . \quad (3.123)$$

The equations of motion are obtained by equating the force $\int \rho \ddot{u}_\alpha dV$ to the force $\int_F \sum_\beta \sigma_{\alpha\beta} dF_\beta$; here V is the volume, F the surface of the crystal and

dF_β is the surface element perpendicular to the direction β . According to the theorem of Gauss,

$$\int \sum_{\beta} \sigma_{\alpha\beta} dF_{\beta} = \int_V \sum_{\beta} \sigma_{\alpha\beta} |_{\beta} dV , \quad (3.124)$$

one obtains $\rho \ddot{u}_\alpha = \sum_{\beta} \sigma_{\alpha\beta} |_{\beta}$, where $\sigma_{\alpha\beta} |_{\beta} = \partial \sigma_{\alpha\beta} / \partial x_{\beta}$. Using these equations and (3.122,120) we obtain

$$\rho \ddot{u}_\alpha = \sum_{\beta\gamma\lambda} C_{\alpha\beta,\gamma\lambda} u_{\gamma} |_{\lambda\beta} = \sum_{\beta\gamma\lambda} C_{\alpha\gamma,\beta\lambda} u_{\beta} |_{\gamma\lambda} . \quad (3.125)$$

The equations of motion (3.125) can easily be solved by considering plane wave solutions for $\vec{u}(\vec{x}, t)$ (Problem 3.8.5). From (3.119,120, and 122), it follows that the elastic tensor $C_{\alpha\beta,\gamma\lambda}$ is symmetric under the transpositions $\alpha \leftrightarrow \beta$ or $\gamma \leftrightarrow \lambda$. Furthermore, from (3.123) it follows that $C_{\alpha\beta,\gamma\lambda}$ is also invariant under the transposition $\alpha\beta \leftrightarrow \gamma\lambda$. Hence, the following relations hold

$$C_{\alpha\beta,\gamma\lambda} = C_{\beta\alpha,\gamma\lambda} = C_{\alpha\beta,\lambda\gamma} = C_{\gamma\lambda,\alpha\beta} . \quad (3.126)$$

This leaves us with 21 independent components, just as for the quantities $\tilde{C}_{\alpha\beta,\gamma\lambda}$. A further reduction of the number of independent components is possible if the invariance of the elastic energy density w [given by (3.123)] against the symmetry operations of the crystal is used. In the case of cubic crystals there are only three independent elastic constants [3.1,19, 21].

We now establish a relation between the elastic constants $C_{\alpha\beta,\gamma\lambda}$ and the quantities $\tilde{C}_{\alpha\beta,\gamma\lambda}$. Comparison of (3.115) with (3.125) shows that the tensors \tilde{C} and C cannot be directly identified because they enter differently into the two equations. However, since $u_{\gamma} |_{\lambda\beta} = u_{\gamma} |_{\beta\lambda}$ and $\tilde{C}_{\alpha\beta,\gamma\lambda} = \tilde{C}_{\alpha\beta} |_{\lambda\gamma}$, we obtain the following relation from (3.115,125):

$$C_{\alpha\gamma,\beta\lambda} + C_{\alpha\lambda,\beta\gamma} = 2\tilde{C}_{\alpha\beta,\gamma\lambda} . \quad (3.127)$$

Applying (3.126) to (3.127), we note that (3.127) implies $\tilde{C}_{\alpha\beta,\gamma\lambda} = \tilde{C}_{\gamma\lambda,\alpha\beta}$ which are the Huang conditions (3.118). Equation (3.127) can be written in the form

$$C_{\alpha\gamma,\beta\lambda} + C_{\alpha\lambda,\gamma\beta} = 2\tilde{C}_{\alpha\beta,\gamma\lambda} .$$

Permutation of $\alpha \leftrightarrow \gamma$ gives

$$C_{\alpha\gamma,\beta\lambda} + C_{\gamma\lambda,\alpha\beta} = 2\tilde{C}_{\gamma\beta,\alpha\lambda} .$$

Permutation of $\alpha \leftrightarrow \beta$ in the latter equation yields

$$C_{\beta\gamma,\lambda\alpha} + C_{\gamma\lambda,\alpha\beta} = 2\tilde{C}_{\gamma\alpha,\lambda\beta} .$$

Adding the first two equations and subtracting the latter one gives

$$C_{\alpha\gamma,\beta\lambda} = \tilde{C}_{\alpha\beta,\gamma\lambda} + \tilde{C}_{\gamma\beta,\alpha\lambda} - \tilde{C}_{\gamma\alpha,\lambda\beta} . \quad (3.128)$$

This equation relates the elastic constants to the atomic force constants via (3.116). Due to the occurrence of the products $r_{\ell\gamma} r_{\ell\lambda}$ in the sum of (3.116), the quantities $C_{\alpha\beta,\gamma\lambda}$ are particularly sensitive to long-range forces, that is, the (small) force constants $\Phi_{\alpha\beta}(0\ell)$ coupling two distant atoms have a comparatively large weight in the expression of the elastic constants. Physically, this is understandable, since for large wavelengths λ , appreciable relative displacements occur only between atoms separated by a large distance, of the order of $\lambda/2$.

Some economy in notation is achieved by pairing the first two and the second two indices in $C_{\alpha\beta,\gamma\lambda}$ and $\tilde{C}_{\alpha\beta,\gamma\lambda}$ and using the equivalence 11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3, 23, 32 \rightarrow 4, 31, 13 \rightarrow 5, and 12, 21 \rightarrow 6. For cubic crystals, the following relations between the elastic constants hold: $C_{11} = C_{22} = C_{33}$, $C_{12} = C_{13} = C_{23} = C_{31} = C_{32}$, and $C_{44} = C_{55} = C_{66}$; all other components are zero. The independent elastic constants are taken to be C_{11} , C_{12} , and C_{44} .

The *bulk modulus* is defined by

$$BM = (C_{11} + 2C_{12})/3 , \quad (3.129a)$$

and the *compressibility* by

$$\kappa = 1/BM . \quad (3.129b)$$

Table 3.2 contains elastic constants of some representative cubic crystals.

Using (3.128) and (3.116), it is possible to express the elastic constants in terms of the atomic force constants. For the case of the fcc lattice with nearest-neighbour interactions, we obtain from Table F.1 (putting $\beta' = -F$, $\gamma' = -G$, and $\alpha' = -H$)

$$\begin{aligned} C_{11} &= \tilde{C}_{11} = \frac{4}{a} F \\ C_{12} &= 2\tilde{C}_{44} - \tilde{C}_{12} = -\frac{2}{a} (F - 2G + H) \\ C_{44} &= \tilde{C}_{12} = \frac{2}{a} (F + H) , \end{aligned} \quad (3.130)$$

Table 3.2. Elastic constants for some cubic crystals at 300 K [3.22].
Elastic constants in 10^{12} dynes/cm²

Crystal	C_{11}	C_{12}	C_{44}
Na	0.0739	0.0622	0.0419
Pb	0.481	0.408	0.146
Al	1.09	0.63	0.28
Ag	1.23	0.92	0.453
W	5.17	2.03	1.57
Ge	1.29	0.49	0.668
Si	1.65	0.64	0.793
Diamond	10.76	1.25	5.76
CsI	0.245	0.066	0.063
CsBr	0.307	0.084	0.075
RbCl	0.365	0.065	0.048
KCl	0.406	0.067	0.063
NaCl	0.487	0.126	0.127
BaF_2	0.904	0.406	0.253
MgAl_2O_4	2.79	1.53	1.53

where a is the lattice constant. From (3.130), the force constants F , G , and H can be calculated if the three elastic constants C_{11} , C_{12} , and C_{44} are known.

At the end of this section, we will consider the special case of *central forces* which means that the potential energy between two atoms, say 0 and ℓ , depends only on the distance R_ℓ between them: $\varphi = \varphi(R_\ell)$. In Appendix J, we calculate the force constants for central forces; for a Bravais lattice the result is

$$\Phi_{\alpha\beta}(0\ell) = - F(\ell) r_{\ell\alpha} r_{\ell\beta} - \delta_{\alpha\beta} G(r_\ell) , \quad (3.131)$$

where r_ℓ is the equilibrium distance between the atoms 0 and ℓ and

$$F(r_\ell) = \frac{1}{r_\ell^2} [\varphi''(r_\ell) - r_\ell^{-1} \varphi'(r_\ell)] , \quad (3.131a)$$

$$G(r_\ell) = r_\ell^{-1} \varphi'(r_\ell) \quad (3.131b)$$

$$\varphi'(r_\ell) = \left(\frac{\partial \varphi}{\partial R_\ell} \right)_{R_\ell} , \quad \varphi''(r_\ell) = \left(\frac{\partial^2 \varphi}{\partial R_\ell^2} \right)_{R_\ell} . \quad (3.131c)$$

Substituting (3.131) in (3.116), one obtains

$$\tilde{C}_{\alpha\beta,\gamma\lambda} = \frac{1}{2V_a} \sum_\ell F(r_\ell) r_{\ell\alpha} r_{\ell\beta} r_{\ell\gamma} r_{\ell\lambda} + \frac{\delta_{\alpha\beta}}{2V_a} \sum_\ell G(r_\ell) r_{\ell\gamma} r_{\ell\lambda} . \quad (3.132)$$

We now require that the lattice be in equilibrium under the action of central forces. Let Φ_{uc} be the potential energy per unit cell. Φ_{uc} depends on the geometry of the unit cell which is defined by the components a_{ij} of the primitive lattice vectors \vec{a}_i . The equilibrium condition at $T = 0$ is (see also Sect. 4.1)

$$\left(\frac{\partial \Phi_{uc}}{\partial a_{ij}} \right)_0 = 0 . \quad (3.133)$$

Φ_{uc} is given by

$$\Phi_{uc} = \frac{1}{2} \sum_{\ell} \varphi(r_{\ell}) . \quad (3.134)$$

Writing $r_{\ell Y} = \sum_i \ell_i a_{iY}$ (ℓ_i = integers), it is easily shown that the condition (1.133), together with (3.134), requires that the second sum in (3.132) which involves the quantities $G(r_{\ell})$, disappears. Therefore, we obtain

$$\tilde{C}_{\alpha\beta,\gamma\lambda} = \frac{1}{2V_a} \sum_{\ell} F(r_{\ell}) r_{\ell\alpha} r_{\ell\beta} r_{\ell\gamma} r_{\ell\lambda} . \quad (3.135)$$

This expression is obviously completely symmetric in all four indices α , β , γ , λ and from (3.128), we obtain the result that for central forces

$$C_{\alpha\beta,\gamma\lambda} = \tilde{C}_{\alpha\beta,\gamma\lambda} . \quad (3.136)$$

The additional relations imposed by the complete symmetry of $C_{\alpha\beta,\gamma\lambda}$ in all four indices are known as the *Cauchy relations*. The Cauchy relations reduce the number of independent elastic constants from 21 to 15 in the general case. They are valid if

- a) every atom is at a center of inversion (which is always the case for a Bravais lattice),
- b) the atoms interact with central forces, and
- c) the lattice is stable under the action of the central forces.

In the case of cubic crystals, the Cauchy relations require that $C_{12} = C_{44}$ so that there are only two independent elastic constants, namely, C_{11} and C_{12} .

The experimental values of the elastic constants for most alkali halides satisfy the Cauchy relations moderately well (Table 3.2). However, from Table 3.2 it is seen that this is not the case for metals. In an alkali metal such as sodium, it is true that the ions are at centers of inversion symmetry and that the screened Coulomb interaction between the ions is a central force; however, the crystal is not in equilibrium under the action

of these forces alone because the kinetic energy of the conduction electrons is a function of volume (Sect.1.3). Therefore, the electron gas contributes to the compressibility, i.e., to $C_{11} + 2C_{12}$ but not to C_{44} or to $(C_{11} - C_{12})/2$ which are the elastic constants describing shearing deformations. Consequently, even the simplest theories do not predict $C_{12} = C_{44}$. The elastic constants of covalent crystals such as Ge, Si and diamond cannot be expected to satisfy the Cauchy relations for several reasons; the most trivial one is that the atoms are not at centers of symmetry.

It is possible to derive relations between the elastic constants and the atomic force constants for crystals with several atoms per unit cell. For a general crystal structure, the expression corresponding to (3.128) is then quite complicated [3.20]. However, if every atom is at a center of inversion, the relation (3.128) still applies but the quantities $\tilde{C}_{\alpha\beta,\gamma\lambda}$ defined in (3.116) are now replaced by the more general expression

$$\tilde{C}_{\alpha\beta,\gamma\lambda} = - \frac{1}{2v_a} \sum_{\kappa\kappa'} \sum_{\ell} \Phi_{\alpha\beta}^{(0\ell)}(K\kappa') r_{\gamma}^{(0\ell)}(K\kappa') r_{\lambda}^{(0\ell)}(K\kappa') . \quad (3.137)$$

Here, $r_{\gamma}^{(0\ell)}(K\kappa')$ is the component of the vector leading from atom $(K\kappa')$ to atom $(K\ell)$, in the direction γ and $\Phi_{\alpha\beta}^{(0\ell)}(K\kappa')$ the corresponding force constants. The relations (3.137) and (3.128) are also valid for ionic crystals in which every ion is at a center of inversion such as the alkali halides. However, in ionic crystals with ions not located at centers of inversion, the situation is more complicated; such crystals are *piezoelectric*, and it is then necessary to account for the macroscopic electric fields which are associated with the deformations [3.20].

Because of anharmonicity, which we discuss in Chap.5, the elastic constants and the atomic force constants are not independent of temperature. For the elastic constants, an increase of 10% or more in going from ordinary temperatures to 0 K is fairly typical.

Measurements of elastic constants by classical methods and ultrasonic pulse methods are described in [3.23,24], respectively. Elastic constants can also be measured by Brillouin scattering or from inelastic neutron scattering techniques [1.35].

3.7 An Illustration: Phonon Dispersion of Monoatomic Crystals with fcc Structure

In this section we discuss the force constants, dynamical matrix and dispersion relations of monoatomic crystals with fcc structure (Fig.3.6a). The primitive rhombohedral unit cell of volume $v_a = a^3/4$ contains one single atom of mass m . There are 12 nearest-neighbour atoms at $\vec{L}_1 = (a/2)(1,1,0)$, etc., and 6 second-nearest-neighbours at $\vec{L}_2 = a(1,0,0)$, etc. The corresponding Brillouin zone is shown in Fig.3.6b. Examples of elements with this structure are the solid rare gases He, Ne, Ar, Kr, Xe and many metals such as Al, Cu, Ni, Pt, Ag, Au.

The dynamical matrix (3.22) is a 3×3 matrix and can be written in the form

$$D_{\alpha\beta}(\vec{q}) = m^{-1} \sum_{\vec{L}} \Phi_{\alpha\beta}(\vec{L}) e^{i\vec{q}\vec{L}} , \quad (3.138)$$

where $\vec{L} = \vec{r}(\ell') - \vec{r}(\ell)$. From (3.17b) it follows that

$$\Phi_{\alpha\beta}(0) = - \sum_{\vec{L} \neq 0} \Phi_{\alpha\beta}(\vec{L}) . \quad (3.139)$$

Substituting (3.139) in (3.138) we obtain

$$D_{\alpha\beta}(\vec{q}) = - 2m^{-1} \sum_{\substack{\vec{L} \\ L \neq 0}} \Phi_{\alpha\beta}(\vec{L}) \sin^2 \frac{\vec{q}\vec{L}}{2} . \quad (3.140)$$

In the following we confine ourselves to nearest-neighbour interactions. According to Table F.1, there are three nonvanishing force constants β' , γ' , and α' ; for convenience we write $\beta' = -F$, $\gamma' = -G$, and $\alpha' = -H$ and obtain from Table F.1

$$\begin{aligned} D_{xx}(\vec{q}) &= \\ &= \frac{4}{m} F \left[\sin^2 \frac{a}{4} (q_x + q_y) + \sin^2 \frac{a}{4} (q_x + q_z) + \sin^2 \frac{a}{4} (q_x - q_y) + \sin^2 \frac{a}{4} (q_x - q_z) \right] \\ &\quad + \frac{4}{m} H \left[\sin^2 \frac{a}{4} (q_y + q_z) + \sin^2 \frac{a}{4} (q_y - q_z) \right] \end{aligned} \quad (3.141)$$

(D_{yy} , D_{zz} from cyclic permutations),

$$D_{xy} = \frac{4}{m} G \left[\sin^2 \frac{a}{4} (q_x + q_y) - \sin^2 \frac{a}{4} (q_x - q_y) \right] \quad (3.142)$$

(D_{yx} , D_{zx} from cyclic permutations).

We consider waves propagating along $\vec{q} = (q_x, 0, 0) = (q, 0, 0)$ and $\vec{q} = (q_x, q_x, 0) = 2^{-1/2}(q, q, 0)$.

a) $\vec{q} = (q, 0, 0)$; from (3.25,141,142) we obtain

$$\omega_L^2(q) = D_{xx} = \frac{16}{m} F \sin^2 \frac{aq}{4}$$

$$\omega_T^2(q) = D_{yy} = D_{zz} = \frac{8}{m} (F + H) \sin^2 \frac{aq}{4}$$

$$D_{xy} = D_{xz} = D_{yz} = 0 \quad (3.143)$$

where ω_L is the frequency of the longitudinal vibration with displacements parallel to \vec{q} , while ω_T is the frequency of the doubly-degenerate transverse vibrations with displacements perpendicular to \vec{q} . From (3.20) the displacement vector of atom ℓ in the mode $(\vec{q})_j$ is

$$\vec{u}(\ell|_j^q) = (Nm)^{-1/2} |A(\vec{q})| \vec{e}_j(\vec{q}) \cos[\vec{q}\vec{r}(\ell) - \omega_j(\vec{q})t + \alpha_j(\vec{q})] . \quad (3.144)$$

In the present case, the polarization vectors $\vec{e}_j(\vec{q})$ are unit vectors independent of \vec{q} and pointing in the x , y , and z -directions. $\vec{r}(\ell) = \vec{\ell}_1 \vec{a}_1 + \vec{\ell}_2 \vec{a}_2 + \vec{\ell}_3 \vec{a}_3$, where the \vec{a}_j are given by (3.49). Figure 3.17a shows the pattern of atomic displacements for the zone boundary vector $\vec{q}_{ZB} = (2\pi/a)(1,0,0)$; this is the X-point in Fig.3.6b.

b) $q = (q_x, q_x, 0) = 2^{-1/2}(q, q, 0)$; from (3.141,142) we obtain

$$\begin{aligned} D_{xx} = D_{yy} &= \frac{4}{m} \left[F \left(\sin^2 \frac{aq}{2\sqrt{2}} + 2 \sin^2 \frac{aq}{4\sqrt{2}} \right) + 2H \sin^2 \frac{aq}{4\sqrt{2}} \right] \\ D_{zz} &= \frac{4}{m} \left(4F \sin^2 \frac{aq}{4\sqrt{2}} + H \sin^2 \frac{aq}{2\sqrt{2}} \right) \\ D_{xy} &= \frac{4}{m} G \sin^2 \frac{aq}{2\sqrt{2}} ; \quad D_{xz} = D_{yz} = 0 . \end{aligned} \quad (3.145)$$

The diagonalization of the two-dimensional submatrix immediately gives

$$\omega_{1,2}^2 = D_{xx} \pm D_{xy} , \quad (3.146)$$

from which we obtain for the transverse vibration polarized in the xy -plane

$$\omega_{T_1}^2(q) = \frac{4}{m} \left[(F - G) \sin^2 \frac{aq}{2\sqrt{2}} + 2(F + H) \sin^2 \frac{aq}{4\sqrt{2}} \right], \quad (3.147)$$

and for the longitudinal vibration

$$\omega_L^2(q) = \frac{4}{m} \left[(F + G) \sin^2 \frac{aq}{2\sqrt{2}} + 2(F + H) \sin^2 \frac{aq}{4\sqrt{2}} \right] \quad (3.148)$$

The eigenvalue of the z-polarized transverse vibration is given by

$$\omega_{T_2}^2(q) = D_{zz} = \frac{4}{m} \left(4F \sin^2 \frac{aq}{4\sqrt{2}} + H \sin^2 \frac{aq}{2\sqrt{2}} \right). \quad (3.149)$$

From (3.28b,145) we obtain

$$\begin{pmatrix} D_{xx} & D_{xy} & 0 \\ D_{xy} & D_{xx} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix} \begin{pmatrix} e_{xj} \\ e_{yj} \\ e_{zj} \end{pmatrix} = \omega_j^2 \begin{pmatrix} e_{xj} \\ e_{yj} \\ e_{zj} \end{pmatrix},$$

where $e_{\alpha j}$ are the components of the eigenvector $\vec{e}_j = \vec{e}(q_j)$. Using ω_j^2 from (3.146,149) gives

$$\begin{aligned} \vec{e}_1 &= \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix} \quad (T_1 - \text{mode}) \\ \vec{e}_2 &= \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (T_2 - \text{mode}) \\ \vec{e}_3 &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \quad (L - \text{mode}) \end{aligned} \quad (3.150)$$

We note that the eigenvectors are again independent of \vec{q} . Furthermore, \vec{e}_1 and \vec{e}_2 are perpendicular to \vec{q} and \vec{e}_3 is parallel to \vec{q} . Hence, the T_1 and T_2 -modes are strictly transverse while the L-mode is strictly longitudinal. The patterns of atomic displacements follow from (3.144,150); they are shown in Fig.3.17b for the wave vector $\vec{q} = (2\pi/a)(1/2, 1/2, 0)$. Note that the zone boundary vector is $\vec{q}_{ZB} = (2\pi/a)(3/4, 3/4, 0)$ which is the K-point in Fig.3.6b.

It can be shown in a similar way that when \vec{q} is parallel to (111), the eigenvectors are still independent of \vec{q} . Thus, when \vec{q} is in certain directions of high symmetry, such as (100), (110) and (111) in a crystal with fcc

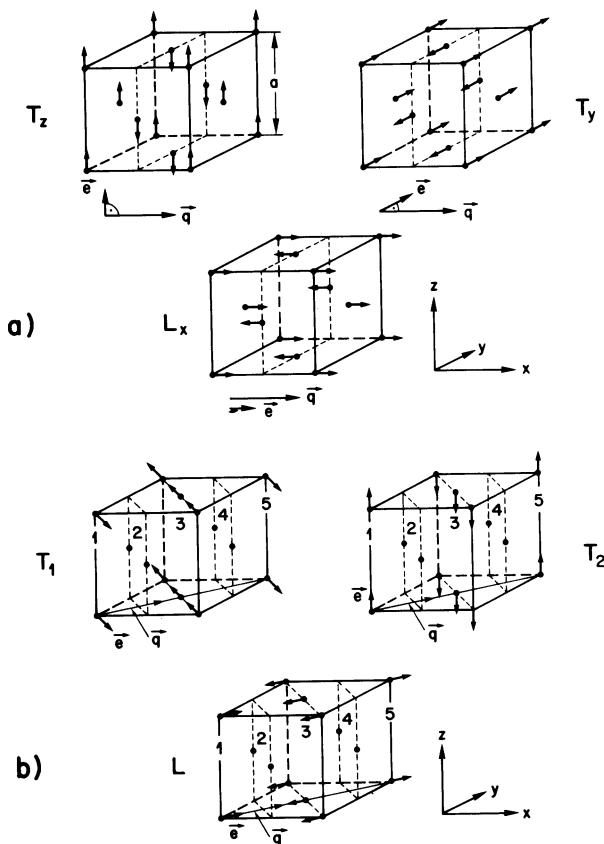


Fig. 3.17. Pattern of atomic displacements in the fcc structure for a) $\vec{q}_{ZB} = (2\pi/a)(1,0,0)$; the entire plane of atoms move in phase and neighbouring planes move in the opposite directions; the wavelength is $\lambda = a$; b) $\vec{q} = (2\pi/a)(1,1,0)$; neighbouring odd-numbered planes move in opposite directions while even-numbered planes are at rest; the wavelength is $\lambda = \sqrt{2}a$

structure, the modes are constrained by symmetry to be purely transverse or purely longitudinal. For a general direction of \vec{q} this is no longer true; the eigenvectors will depend on both the magnitude and the direction of \vec{q} , that is, their orientation relative to \vec{q} depends on the force constants and therefore the modes will not be purely transverse or purely longitudinal.

As an example, we consider the phonon dispersion of aluminium. According to (3.130), the three elastic constants C_{11} , C_{12} , and C_{44} are just sufficient to determine the three force constants F , G , and H . Using the values of the elastic constants quoted in Table 3.2 and $a = 4.04 \text{ \AA}$, we obtain $F = 1.08 \cdot 10^4$

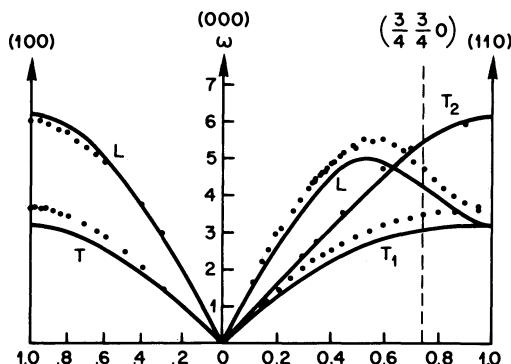


Fig. 3.18. Observed (points) and calculated (full lines) phonon dispersion of aluminium in the (100) and (110)-directions at 300 K. ω in 10^{13} radians per sec against reduced wave vector. The corresponding Brillouin zone is shown in Fig. 3.6b. Calculation: nearest-neighbour interactions with 3 force constants derived from the 3 elastic constants. Experimental values from [3.25]

dynes/cm, $G = 0.89 \cdot 10^4$ dynes/cm, and $H = 0.50 \cdot 10^4$ dynes/cm. From (3.143, 147-149), the phonon dispersion for \vec{q} parallel to the (100) and (110)-directions have been calculated and the results are shown in Fig. 3.18. The agreement with the observed dispersion obtained from inelastic neutron scattering is satisfactory in view of the rather drastic approximations made. The discrepancy at higher values of q is only to be expected and more distant interactions would be needed to obtain better agreement.

3.8 Problems

3.8.1 Brillouin Zone in Two Dimensions

Construct the Brillouin zone for the two-dimensional lattice defined by $\vec{a}_1 = a(1, 0)$, $\vec{a}_2 = a(1/4, 1/2)$ using $\vec{a}_i \vec{b}_j = 2\pi\delta_{ij}$.

3.8.2 Critical Points (c.p.) in the Density of States

Prove that $g_j(\omega) \sim (\omega_c - \omega)^{\frac{1}{2}}$ with $\omega < \omega_c$ for a maximum and $g_j(\omega) \sim (\omega - \omega_c)^{\frac{1}{2}}$ with $\omega > \omega_c$ for a minimum. Use (3.83a, 87). Hint: Equation (3.87) can be written in the form

$$\omega = \omega_c + \sum_i \epsilon_i x_i^2 ,$$

where $x_i = (a_i/\epsilon_i)^{\frac{1}{2}}(q_i - q_{ci})$ and $\epsilon_i = \pm 1$. Since $d^3q \sim d^3x$, it follows that $g_j(\omega)d\omega \sim \int d^3x$. The easiest way to evaluate this expression is to transform the right-hand side so as to make ω one of the variables of integration and then to drop the integration over ω . If the c.p. is a maximum ($\epsilon_i = -1$), this is achieved by the transformation

$$x_1 = (\omega_c - \omega)^{\frac{1}{2}} \sin\vartheta \cos\varphi$$

$$x_2 = (\omega_c - \omega)^{\frac{1}{2}} \sin\vartheta \sin\varphi$$

$$x_3 = (\omega_c - \omega)^{\frac{1}{2}} \cos\vartheta$$

An analogous transformation applies for a minimum ($\epsilon_j = +1$). By evaluating d^3x , calculate $g_j(\omega)$ for a maximum and a minimum. (For a saddle point, more complicated transformations must be introduced [3.9]).

3.8.3 Density of States in Two Dimensions

a) Derive a general expression for the density of states analogous to (3.86) for a two-dimensional lattice.

b) From the expression derived in (a), calculate the Debye density of states $g_D(\omega)$.

Result: $g_D(\omega) \sim \omega$.

3.8.4 Debye Specific Heat in Two Dimensions

Using the results from Problem 3.8.3, calculate the mean energy and the specific heat $c_D(T)$ in the Debye approximation for a two-dimensional lattice.

Result: $c_D(T) \sim T^2$.

3.8.5 Elastic Waves in Continuous Media

Consider a plane wave solution $\vec{u} = \vec{u}_0 \exp[i(\vec{q}\vec{x} - \omega t)]$ to the equation of motion (3.125).

a) Show that the resulting system of homogeneous equations is given by

$$\sum_{\beta} \left(\sum_{\gamma\lambda} C_{\alpha\gamma, \beta\lambda} q_{\gamma} q_{\lambda} - \delta_{\alpha\beta} \rho \omega^2 \right) u_{\beta} = 0 .$$

b) Show that for cubic crystals, the secular determinant is given by

$$\begin{vmatrix} (C_{11}q_1^2 + C_{44}q_2^2 + C_{44}q_3^2 - \rho\omega^2) & (C_{12} + C_{44})q_1q_2 & (C_{12} + C_{44})q_1q_3 \\ (C_{12} + C_{44})q_1q_2 & (C_{11}q_2^2 + C_{44}q_1^2 + C_{44}q_3^2 - \rho\omega^2) & (C_{12} + C_{44})q_2q_3 \\ (C_{12} + C_{44})q_1q_3 & (C_{12} + C_{44})q_2q_3 & (C_{11}q_3^2 + C_{44}q_1^2 + C_{44}q_2^2 - \rho\omega^2) \end{vmatrix} = 0$$

Hint: Use the two-suffix notation and the relations between the elastic constants for cubic crystals discussed in Sect. 3.6.

c) From the results obtained in Problem 3.8.5, show that when $\vec{q} = (q, 0, 0)$, the frequencies of the longitudinal and transverse vibrations are given by $\omega_L^2 = (C_{11}/\rho)q^2$, $\omega_T^2 = (C_{44}/\rho)q^2$, respectively. Show that when $\vec{q} = 2^{-\frac{1}{2}}(q, q, 0)$, the frequency of the x_3 polarized shear wave is given by $\omega_{T1}^2 = (C_{44}/\rho)q^2$. Demonstrate that the waves polarized in the x_1x_2 -plane are given by $\omega_L^2 = (1/2\rho) \times (C_{11} + C_{12} + 2C_{44})q^2$ and $\omega_T^2 = (1/2\rho)(C_{11} - C_{12})q^2$.

3.8.6 Vibrations in Crystals with CsCl Structure

a) From (3.23) and Table F.1, construct the dynamical matrix for CsCl for nearest-neighbour interactions (Fig.3.4). Use (3.17b) and put $\alpha'' = -F$, $\gamma'' = -G$ in Table F.1.

b) Show that when $\vec{q} = (q, 0, 0)$ and $q < \pi/a$, the six-dimensional matrix can be factored into 2×2 matrices corresponding to modes polarized in the x, y and z directions. If $q = \pi/a$, the dynamical matrix factors into 6 one-dimensional matrices. Note that these results are independent of the range of interactions.

c) Show that when $q = (q, 0, 0)$, the eigenvalues are given by

$$\lambda_{1,2} = 4 \frac{F}{\mu} \left[1 \pm \left(1 - \frac{4\mu^2}{m_1 m_2} \sin^2 \frac{aq}{2} \right)^{\frac{1}{2}} \right] ,$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ and a is the lattice parameter. Calculate the eigenvalues for $q = 0$ and $q = \pi/a$. Compare the above expression for $\lambda_{1,2}$ with the corresponding expression (2.36) for the linear NaCl chain.

d) From (3.28b), calculate the ratios of the components of the eigenvectors $e(1|j)/e(2|j)$ for the LA, LO, TA and TO-modes at $\vec{q} = 0$ and $\vec{q}_{ZB} = (\pi/a, 0, 0)$. Make figures of the corresponding patterns of atomic displacements.

4. Interatomic Forces and Phonon Dispersion Curves

Phonon dispersion curves $\omega(\vec{q})$ can be measured by inelastic neutron scattering techniques; this important method will be discussed in [1.35]. The curves determined by experiments are mainly of interest because they provide chance of testing various models of interatomic forces. The forces between the atoms are governed by the electronic structure of the atoms involved, and in simple cases it is possible to derive force constants from "first principles" which are based on the electronic wave functions [4.1-5]. With the exception of some qualitative remarks about metals, we shall not discuss these microscopic models here but consider only certain *phenomenological models* for the interatomic forces. A good model should contain only a few, but physically meaningful, parameters.

The choice of the model depends on the type of binding between the atoms. For the *solid inert gases*, a good model is based on the *Lennard-Jones potential* which describes the weak van der Waals attractive forces and the repulsive forces between pairs of neutral atoms [4.6]. For this case the force constants can be expressed in terms of two parameters; the calculated phonon dispersion curves agree reasonably well with the experiments as will be illustrated for solid Argon [4.7]. In *ionic crystals*, strong Coulomb forces and short-range repulsive forces operate between the ions. In the *rigid-ion model* [4.8-11], the ionic charges are approximated by point charges centered at the nuclei. In reality the ions are not rigid but polarizable. In the course of a lattice vibration, the electric field set up by the displacement of the ions is modified by the *electronic polarizability*; this modifies the forces and affects the phonon frequencies. Allowance for ionic polarizabilities leads to *effective dynamic charges* such as the *Szigeti charge*. The most popular model for ionic crystals with polarizable ions is the *shell model* [4.12-16]: in this model each ion is regarded as being composed of a rigid core and a charged shell which is bound to the core by a spring and

can, therefore, be displaced relative to the core. The shell model will be illustrated for NaI.

While for the solid inert gases and ionic crystals well-established interatomic force law exist, no corresponding expression is known for *covalent crystals* such as diamond, graphite, silicon or germanium. It has, however, been found in practice that the shell model with only a few parameters give quite good agreement with the measurements on germanium. Thus success underlines the similarity, at least in some areas, between ionic and covalent solids. Another model which we shall discuss is the *bond charge model* developed for covalently bonded atoms [4.17,18]. With this model, excellent agreement with experiments has been obtained for germanium with only 4 parameters and for GaAs with only 6 parameters.

A model which is often used for covalent or partly covalent crystals is the *valence force model*. This model has originally been developed for vibrations in molecules [4.19,20] but the formalism can be extended to crystals as well [4.21,22]. The potential energy is expressed in terms of changes in bond distances, bond angles and other so-called *internal coordinates*. We shall illustrate this model for the linear $(SN)_X$ chain and discuss the results for diamond and β -AgI.

In molecular crystals or crystals containing complex ions, it is often possible to separate the *internal vibrations* within the molecules from their *external vibrations* [4.23]. External vibrations are translational or librational motions of the whole molecules or complex ions which are regarded as being rigid units. If the separation between internal and external vibrations is possible, the problem can be greatly simplified. We shall illustrate the external vibrations for a simple one-dimensional system and for $(ND_4)Cl$.

The theory of phonons in metals involves the electron-phonon interaction and, strictly speaking, lies outside the scope of this book. Nevertheless, we give a qualitative discussion of this topic which serves to illustrate the essential physics such as the screening of the ions by the conduction electrons. This screening is responsible for the *Kohn anomaly* observed in some dispersion curves, an effect which is particularly pronounced in one-dimensional metals [1.35].

4.1 Lattice Dynamics of the Solid Inert Gases

The inert gases Ne, Ar, Kr, Xe which form one of the classic types of solid, crystallize in the fcc structure. An exception is helium for which the atomic mass is so small that the quantum mechanical zero-point motion prevents it from solidifying at all, unless an external pressure is imposed. For this reason, solid helium is called a *quantum crystal*. Since in solid helium the displacements of the atoms are very large, anharmonic effects are of prime importance.

In the following we consider the lattice dynamics of the heavier inert gases (especially Ar, Kr and Xe) in the harmonic approximation at zero temperature. Although the inert gas atoms have closed-shell electron configurations, the solution of the quantum mechanical problem leading to an interatomic potential energy is not really possible at present. Therefore, more or less empirical potentials have to be assumed. The commonly-used form for inert gases is a central two-body potential energy of the form

$$\varphi(r) = -\frac{A}{r^6} + \frac{B}{r^n} , \quad (4.1)$$

where r is the distance between the atoms, and A , B and n are parameters with n around 12. The first term represents the van der Waals attraction which originates from fluctuating dipole forces. The van der Waals interaction term can be derived quantum mechanically [4.24,25]. The second term represents the repulsive interaction: as the two atoms are brought together, their charge distributions gradually overlap and at sufficiently small separations, the overlap energy is repulsive, mainly because of the Pauli exclusive principle. This term is difficult to derive quantum mechanically, mainly because of exchange effects. Choosing $n = 12$ and defining $\sigma = (B/A)^{1/6}$ and $\epsilon = A^2/4B$, we obtain from (4.1)

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] . \quad (4.2)$$

This is the *Lennard-Jones 6-12 potential energy* which is displayed in Fig. 4.1. ϵ is the minimum of the potential energy, $\varphi(\sigma) = 0$, and the separation at the minimum is $r_m = 2^{1/6}\sigma$. The two parameters σ and ϵ can be determined from the observed lattice constant a_0 and the heat of sublimation $-L_0$, respectively, at $T = 0$. For this purpose we consider the free energy

$$F = U - TS . \quad (4.3)$$

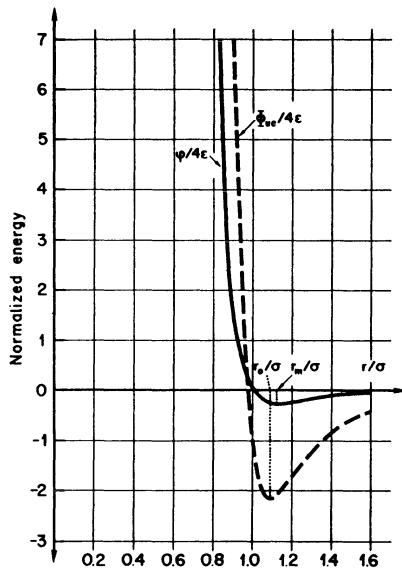


Fig.4.1. The solid line shows the Lennard-Jones potential according to (4.2). The dashed line illustrates the static potential energy per unit cell, Φ_{uc} , of the fcc lattice according to (4.10)

U is the internal energy and S is the entropy. U is given by

$$U = \Phi_0 + \bar{E}(T) , \quad (4.4)$$

where Φ_0 is the static energy of the crystal and $\bar{E}(T)$ is the mean vibrational energy given by (2.128). At $T = 0$ we obtain from (2.129) and (4.3)

$$F = \Phi_0 + \frac{1}{2} \sum_s \hbar \omega_s . \quad (4.5)$$

The second term represents the zero-point energy which we shall neglect in the following. This is a reasonable approximation for Ar, Kr, and Xe but the approximation breaks down for Ne and especially for He. We therefore obtain

$$F \approx \Phi_0 = N\Phi_{\text{uc}} , \quad (4.6)$$

where N is the number of unit cells and Φ_{uc} is the static potential energy per unit cell. For a monoatomic lattice

$$\Phi_{\text{uc}} = \frac{1}{2} \sum_l \varphi(r_l) , \quad (4.7)$$

where $\varphi(r_l)$ is the interaction energy between the central atom in the unit cell considered and the atom at position \vec{r}_l . The equilibrium volume V_0 occupied by the crystal is given by the *equation of state* which connects the pressure P , the volume V and the temperature T :

$$P = - \left(\frac{\partial F}{\partial V} \right)_T . \quad (4.8)$$

As we desire the volume under normal pressures which have negligible effects on solids, we can put $P = 0$ and at $T = 0$, we obtain from (4.8) and (4.6)

$$\left(\frac{\partial \Phi_{uc}}{\partial v} \right)_{v_0} = \left(\frac{\partial \Phi_{uc}}{\partial r} \right)_{r_0} = 0 , \quad (4.9)$$

where v and r are the volume of the unit cell and the nearest-neighbour separation, respectively, and v_0 and $r_0 = a_0/\sqrt{2}$ are the corresponding equilibrium values at $T = 0$. Defining $r_\ell = p_\ell r$, we obtain from (4.2,7)

$$\Phi_{uc}(r) = 2\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} S_{12} - \left(\frac{\sigma}{r} \right)^6 S_6 \right] \quad (4.10)$$

with $S_{12} = \sum_\ell p_\ell^{-12}$ and $S_6 = \sum_\ell p_\ell^{-6}$. These sums converge rapidly and for the fcc lattice one obtains $S_{12} = 12.131$ and $S_6 = 14.454$. Differentiating (4.10) with respect to r , we obtain from (4.9)

$$\sigma = \left(\frac{S_6}{2S_{12}} \right)^{1/6} r_0 = 0.917 r_0 = 0.648 a_0 . \quad (4.11)$$

Substituting σ/r_0 from (4.11) in (4.10), the static lattice energy per particle is given by

$$\Phi_{uc}(r_0) = - \frac{1}{2} \frac{S_6^2}{S_{12}} \varepsilon = - 8.63 \varepsilon . \quad (4.12)$$

Identifying $\Phi_{uc}(r_0)$ with the experimental heat of sublimation $-L_0$, we obtain

$$\varepsilon = \frac{L_0}{8.63} . \quad (4.13)$$

The potential energy $\Phi_{uc}(r)$ for the fcc lattice is shown in Fig.4.1. Table 4.1 contains experimental values of r_0 , L_0 , σ , and ε . It is seen that for the heavier inert gases Ar, Kr, and Xe, these values agree well with the corresponding crystal data.

Having established the form of the potential energy and its parameters σ and ε , we now evaluate the dynamical matrix $D(\vec{q})$ and the phonon frequencies $\omega_j(\vec{q})$. According to (3.140), the dynamical matrix for a monoatomic crystal with atomic mass m is given by

Table 4.1. Experimental values of nearest-neighbour distances r_0 , heats of sublimation L_0 and the Lennard-Jones parameters σ and ϵ at $T = 0$ [4.26]. Values in parenthesis from gas phase data [4.27]

	$r_0 [\text{\AA}]$	$L_0 \left[\frac{\text{eV}}{\text{atom}} \right]$	$\sigma [\text{\AA}]$	$\epsilon \left[\frac{\text{eV}}{\text{atom}} \right]$
Ne	3.13	0.02	2.87 (2.74)	0.0023 (0.0031)
Ar	3.75	0.08	3.44 (3.40)	0.0093 (0.0104)
Kr	3.99	0.11	3.66 (3.65)	0.0128 (0.0140)
Xe	4.33	0.17	3.97 (3.98)	0.0198 (0.0200)

$$D_{\alpha\beta}(\vec{q}) = -2m^{-1} \sum_{\ell \neq 0} \Phi_{\alpha\beta}(0\ell) \sin^2\left(\frac{\vec{q}\vec{r}_\ell}{2}\right), \quad (4.14)$$

where $\Phi_{\alpha\beta}(0\ell)$ are the force constants belonging to the pair of atoms in unit cells 0 and ℓ . Since the Lennard-Jones potential is based on central forces, the force constants can be calculated with the results outlined in Appendix J. For the elements of the dynamical matrix one then obtains

$$D_{\alpha\beta}(\vec{q}) = \frac{32\epsilon}{a^2 m n} \left[\left(\frac{6b_0^6}{|\vec{n}|^8} - \frac{6b_0^{12}}{|\vec{n}|^{14}} \right) \delta_{\alpha\beta} - \left(\frac{48b_0^6}{|\vec{n}|^{10}} - \frac{168b_0^{12}}{|\vec{n}|^{16}} \right) n_\alpha n_\beta \right] \sin^2\left(\frac{\vec{q}\vec{r}_n}{2}\right). \quad (4.15)$$

Here, $\vec{n} = (n_1, n_2, n_3)$ is the vector defined by $\vec{r}_n = a\vec{n}/2$, where \vec{r}_n is the equilibrium position of atom n and n_1, n_2, n_3 are any integers subject to the condition that the sum $n_1 + n_2 + n_3$ is even for the fcc lattice.

$b_0 = 2\sigma/a_0 = 1.297$ according to (4.11). The sums appearing in (4.15) converge rapidly and have been evaluated numerically by GRINDLAY and HOWARD [4.6]. The secular equation is a 3×3 determinant of the form

$$|D_{\alpha\beta}(\vec{q}) - \delta_{\alpha\beta}\omega^2(\vec{q})| = 0. \quad (4.16)$$

Results were evaluated in the form of a reduced frequency

$$\nu_{\text{red}}(\vec{q}) = \frac{1}{2} a_0 \left(\frac{m}{8\epsilon} \right)^{1/2} \omega(\vec{q}). \quad (4.17)$$

Phonon dispersion curves have been measured for ^{36}Ar at 10 K [4.7]. In Fig.4.2, the experiments are compared with the theoretical dispersion curves which are based on the parameters listed in Table 4.1. The agreement is sa-

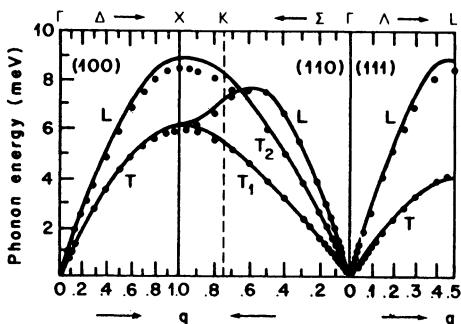


Fig. 4.2. Phonon dispersion curves for ^{36}Ar (experimental points [4.7]). The solid lines are calculated on the basis of (4.17) and the parameters listed in Table 4.1

tisfactory in view of the fact that the model contains only two parameters. However, the calculated phonon energies are systematically higher than the experimental points, especially for the high-energy phonons. Some reduction of this discrepancy might be achieved by including the anharmonic effects (Chap. 5) relevant at 10 K. Furthermore, we have neglected the effect of the zero-point motion on the lattice spacing. It should also be emphasized that we have chosen the Lennard-Jones 6-12 potential, *not* because it is the best representation of the interatomic forces, but because it is simple and serves to illustrate some of the essential features. More refined models which include anharmonic corrections have been used for the solid inert gases [4.28-31].

From the force constants derived from the Lennard-Jones 6-12 potential together with (3.136) and (3.116), the following expressions for the elastic constants are obtained: $C_{11} = 105.3\epsilon/\sigma^3$; $C_{12} = C_{44} = 60.18\epsilon/\sigma^3$ [4.6]. For Ar the numbers are: $C_{11} = 385 \times 10^8$ dynes/cm 2 , $C_{12} = C_{44} = 220 \times 10^8$ dynes/cm 2 . On the other hand, from small wave vector phonon data, the following experimental values are deduced: $C_{11} = (421 \pm 8) \times 10^8$, $C_{12} = (227 \pm 9) \times 10^8$, and $C_{44} = (217 \pm 6) \times 10^8$ dynes/cm 2 [4.7]. The agreement is satisfactory and the Cauchy relations ($C_{12} = C_{44}$) are nearly satisfied; this suggests that the magnitude of noncentral interactions in Ar are small (Sect. 3.6).

4.2 The Rigid-Ion Model for Ionic Crystals

4.2.1 Definition of the Model and Dynamical Matrix

In the rigid-ion model, an ion of type κ carries a point charge $z_\kappa e$, where e is the magnitude of the electronic charge; thus, the ions are not polarizable. The interaction energy of two ions $i = (\overset{\circ}{\underset{\circ}{\kappa}})$ and $k = (\overset{\circ}{\underset{\circ}{\kappa'}}$) separated by a distance R_{ik} is

$$\varphi(R_{ik}) = \varphi^{(R)}(R_{ik}) + \varphi^{(C)}(R_{ik}) , \quad (4.18)$$

where $\varphi^{(R)}$ is the repulsive or overlap energy usually approximated by the Born-Mayer potential given by

$$\varphi^{(R)}(R_{ik}) = b_{ik} e^{-R_{ik}/\rho} , \quad (4.19)$$

and $\varphi^{(C)}$ is the Coulomb energy

$$\varphi^{(C)}(R_{ik}) = \frac{z_i z_k e^2}{R_{ik}} . \quad (4.20)$$

Instead of (4.19), the repulsive energy could also be approximated by an expression of the form B/R^n as has been used for the solid inert gases (Sect.4.1). In any case, $\varphi^{(R)}$ is a short-range energy which in a first approximation may be extended to nearest-neighbour ions only. On the other hand, $\varphi^{(C)}$ represents the long-range Coulomb forces and it is this term which will complicate the lattice dynamical problem considerably.

Since we are dealing with central forces, the force constants can be obtained directly from Appendix J. According to (4.18) and (J.4 and 7), the total force constants are

$$\Phi_{\alpha\beta}(ik) = \varphi_{\alpha\beta}^{(R)}(ik) + \varphi_{\alpha\beta}^{(C)}(ik) . \quad (4.21)$$

$\varphi_{\alpha\beta}^{(R)}(ik)$ and $\varphi_{\alpha\beta}^{(C)}(ik)$ are the force constants derived from the repulsive and Coulomb energy, respectively. For convenience, we introduced dimensionless short-range parameters A_{ik} and B_{ik} defined by

$$\varphi^{(R)''}(r_{ik}) = \frac{b_{ik}}{\rho^2} e^{-r_{ik}/\rho} = \frac{e^2}{2v_a} A_{ik} , \quad (4.22a)$$

$$\frac{1}{r_{ik}} \varphi^{(R)'}(r_{ik}) = -\frac{b_{ik}}{r_{ik}\rho} e^{-r_{ik}/\rho} = \frac{e^2}{2v_a} B_{ik} , \quad (4.22b)$$

where r_{ik} is the equilibrium distance between the ions i and k and v_a is the volume of the primitive unit cell defined by (3.37). From (J.11-13), we then obtain for $i \neq k$

$$\varphi_{\alpha\beta}^{(R)}(ik) = -\frac{e^2}{2v_a} \left[(A_{ik} - B_{ik}) \frac{r_{ik\alpha} r_{ik\beta}}{r_{ik}^2} + \delta_{\alpha\beta} B_{ik} \right] , \quad (4.23a)$$

while according to (3.17b)

$$\Phi_{\alpha\beta}^{(R)}(ii) = - \sum_k \Sigma_{\alpha\beta}^{(R)}(ik) . \quad (4.23b)$$

Similarly, we obtain for the force constants of the Coulomb forces for $i \neq k$

$$\Phi_{\alpha\beta}^{(C)}(ik) = z_i z_k e^2 \frac{\delta_{\alpha\beta} r_{ik}^2 - 3r_{ik\alpha} r_{ik\beta}}{r_{ik}^5} . \quad (4.24a)$$

and

$$\Phi_{\alpha\beta}^{(C)}(ii) = - \sum_k \Phi_{\alpha\beta}^{(C)}(ik) . \quad (4.24b)$$

It is convenient to write the atomic displacements in the form

$$\vec{u}_{(\kappa|j)}^{(\ell)} = \sum_{\vec{q}_j} \vec{u}_{(\kappa|j)} \exp\{i[\vec{q}\vec{r}_{(\kappa)}^{(\ell)} - \omega_j(\vec{q})t]\} . \quad (4.25)$$

$\vec{u}_{(\kappa|j)}$ is the amplitude of atom κ in the mode (\vec{q}_j) . Substitution of (4.25) in (3.15) gives

$$\omega_{mu}^2 = Mu . \quad (4.26)$$

Here, m is a diagonal matrix whose diagonal elements are the masses m_{κ} and u is a column matrix containing $3n$ elements. For practical purposes, it is convenient to introduce a modified dynamical matrix M defined by

$$M_{\alpha\beta}^{(\vec{q})} = \sum_{\ell} \Phi_{\alpha\beta}^{(\ell\ell')} \exp\{i\vec{q}[\vec{r}_{(\kappa')}^{(\ell')} - \vec{r}_{(\kappa)}^{(\ell)}]\} \quad (4.27)$$

and the secular equation is

$$|M(\vec{q}) - m\omega^2(\vec{q})| = 0 . \quad (4.28)$$

Substituting (4.21) in (4.27), we can write

$$M = R + ZCZ \quad (4.29)$$

and (4.26) can be written in the form

$$\omega_{mu}^2 = Ru + ZCZu . \quad (4.30)$$

$R(\vec{q})$ is the matrix of the repulsive forces defined by

$$R_{\alpha\beta}^{(\vec{q})} = \sum_{\ell} \Phi_{\alpha\beta}^{(R)}(\ell\ell') \exp\{i\vec{q}[\vec{r}_{(\kappa')}^{(\ell')} - \vec{r}_{(\kappa)}^{(\ell)}]\} , \quad (4.31)$$

while $C(\vec{q})$ is the Coulomb matrix, the elements of which are defined by

$$z_{\kappa} z_{\kappa'} C_{\alpha\beta}^{(\vec{q})} = \sum_{\ell} \Phi_{\alpha\beta}^{(C)}(\ell\ell') \exp\{i\vec{q}[\vec{r}_{(\kappa')}^{(\ell')} - \vec{r}_{(\kappa)}^{(\ell)}]\} . \quad (4.32)$$

There is no difficulty in evaluating the repulsive matrix $R(\vec{q})$ since the series (4.31) converges rapidly. An example will be given below for NaCl. However, some care is required in evaluating the expression (4.32); because of the long-range nature of the Coulomb potential, the series is only conditionally convergent.

4.2.2 Coulomb Matrix and Electric Fields

It is not feasible to evaluate the series (4.32) directly; in fact, it does not tend to a unique value as $\vec{q} \rightarrow 0$, but to a value which depends on the relative directions of \vec{q} and the electrical polarization associated with the mode concerned. Fortunately, there is a very elegant procedure, known as EWALD's method [4.32], by which $C(\vec{q})$ can be expressed as the sum of two rapidly convergent series, one involving a summation over a limited region in the reciprocal lattice and the other over a limited region in the direct lattice. Let $\varphi^{(G)}(\frac{R}{\kappa\kappa'})$ be the potential energy of a point charge $z_{\kappa}e$ at a point \vec{R} in a three-dimensional Gaussian charge distribution

$$\varphi^{(G)} = z_{\kappa}e(\frac{\eta}{\pi})^{3/2}e^{-\eta R^2} \quad (4.33)$$

which contains the total charge $z_{\kappa}e$ (Fig. 4.3). The energy of two point charges $z_{\kappa}e$ and $z_{\kappa'}e$ separated by \vec{R} would be $\varphi^{(C)}(\frac{R}{\kappa\kappa'}) = z_{\kappa}z_{\kappa'}e^2/R$. Now we write $\varphi^{(C)}$ in the form

$$\varphi^{(C)} = \varphi^{(G)} + [\varphi^{(C)} - \varphi^{(G)}] = \varphi^{(G)} + \varphi^{(H)} . \quad (4.34)$$

$\varphi^{(H)}$ can be evaluated from elementary electrostatics and is (Appendix K)

$$\varphi^{(H)}(\frac{R}{\kappa\kappa'}) = 2z_{\kappa}z_{\kappa'} \frac{e^2}{R} (\frac{\eta}{\pi})^{1/2} \int_0^{\infty} e^{-\eta R'^2} dR' . \quad (4.35)$$

The particular choice of a Gaussian charge distribution is made for mathematical convenience and $\varphi^{(C)}$ is, of course, independent of the parameter η . In Appendix K, we derive an explicit expression for $C(\vec{q})$ using the \vec{Q} -space representation and EWALD's transformation. The result is

$$z_{\kappa}z_{\kappa'}C_{\alpha\beta}(\frac{\vec{q}}{\kappa\kappa'}) = N_{\alpha\beta}(\frac{\vec{q}}{\kappa\kappa'}) - \delta_{\kappa\kappa'} \sum_{\kappa''} N_{\alpha\beta}(\frac{0}{\kappa\kappa'}) , \quad (4.36)$$

where

$$N_{\alpha\beta}(\frac{\vec{q}}{\kappa\kappa'}) = N_{\alpha\beta}^{(G)}(\frac{\vec{q}}{\kappa\kappa'}) + N_{\alpha\beta}^{(H)}(\frac{\vec{q}}{\kappa\kappa'}) . \quad (4.37)$$

In (4.37), the matrix $N^{(G)}(\vec{q})$ is defined by

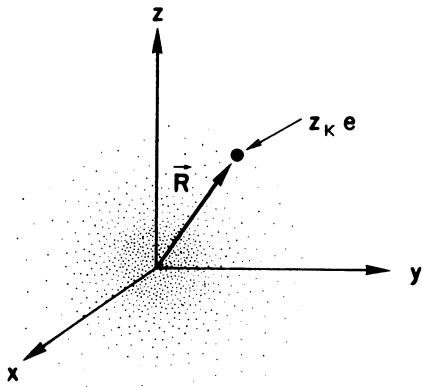


Fig.4.3. Three-dimensional Gaussian charge distribution centered at the origin interacting with a point charge $z_k e$ at the point \vec{R}

$$N_{\alpha\beta}^{(G)}(\vec{q}) = 4\pi z_k z_{k'} \frac{e^2}{\sqrt{a}} \sum_{\vec{\tau}} \frac{(\vec{\tau} + \vec{q})_\alpha (\vec{\tau} + \vec{q})_\beta}{|\vec{\tau} + \vec{q}|^2} e^{i\vec{\tau}[\vec{r}(k) - \vec{r}(k')]} \exp(-|\vec{\tau} + \vec{q}|^2/4n) , \quad (4.38)$$

while the elements of the correction term $N^{(H)}(\vec{q})$ are given by

$$N_{\alpha\beta}^{(H)}(\vec{q}) = - \sum_{\ell'} \left(e^{i\vec{q}\vec{R}} \frac{\partial^2 \varphi^{(H)}(\vec{R})}{\partial R_\alpha \partial R_\beta} \right)_{\vec{R}=\vec{r}(k') - \vec{r}(\ell')} . \quad (4.39)$$

The sum in (4.38) extends over the reciprocal lattice points $\vec{\tau}$ and originates from $\varphi^{(G)}$. On the other hand, $N_{\alpha\beta}^{(H)}(\vec{q})$ is expressed as a sum in crystal space and depends on $\varphi^{(H)}$. $N(\vec{q})$ defined by (4.37) is, of course, independent of the parameter n . A value of n of the order of r_0^{-2} , where r_0 is the nearest-neighbour distance between the ions, gives rapid convergence for both series. It is, however, also possible to choose $n \gg r_0^{-2}$ which means that the charge distribution (4.33) is very narrow and its overlap with the point charge $z_k e$ is negligible. With this choice, the correction term (4.39) can be made negligible but the series in (4.38) then converges rather slowly [4.10,33].

We are now in a position to introduce the Coulomb field and the polarization. Instead of (4.30) we write

$$\omega_{mu}^2 = Ru - eZE^{(C)} , \quad (4.40)$$

where the second term on the right-hand side of this equation represents the force on the ions due to the total Coulomb field $E^{(C)}$. In (4.40), $E^{(C)}$ is a $3n$ -dimensional column vector whose components are the amplitudes

$E_{\alpha}^{(C)}(\kappa|\vec{q})$ ($\alpha = 1, 2, 3; \kappa = 1 \dots n$). Comparing (4.40) with (4.30), we obtain

$$E^{(C)} = -\frac{1}{e} CZu . \quad (4.41)$$

or written out explicitly

$$E_{\alpha}^{(C)}(\kappa|\vec{q}) = -\frac{1}{e^2} \sum_{\kappa' \beta} C_{\alpha\beta}(\kappa|\vec{q}) z_{\kappa'} e u_{\beta}(\kappa'|\vec{q}) . \quad (4.42)$$

The form (4.42) illustrates that the Coulomb field $E^{(C)}$ is a *dipole field*: when an ionic charge $z_{\kappa'} e$ is displaced by $u_{\beta}(\kappa'|\vec{q})$, the net effect is as though a charge $-z_{\kappa'} e$ has been placed at the undisplaced position of the ion to annihilate the original charge. The two charges $-z_{\kappa'} e$ and $z_{\kappa'} e$ form a dipole moment; the displacement is thus equivalent to the addition of a *displacement dipole moment* $z_{\kappa'} e u_{\beta}(\kappa'|\vec{q})$. Thus, $E_{\alpha}^{(C)}(\kappa|\vec{q})$ is the amplitude of the total dipole field at site κ (α component) due to the displacement dipoles at all sites κ' created in the mode (\vec{q}) . The amplitude of the *polarization* produced by the displacement of ions of type κ' in the mode (\vec{q}) is, by definition, the dipole moment per unit volume v_a :

$$P_{\beta}(\kappa'|\vec{q}) = \frac{1}{v_a} z_{\kappa'} e u_{\beta}(\kappa'|\vec{q}) . \quad (4.43)$$

Substituting (4.43) in (4.42) gives

$$E_{\alpha}^{(C)}(\kappa|\vec{q}) = -\frac{v_a}{e^2} \sum_{\kappa' \beta} C_{\alpha\beta}(\kappa|\vec{q}) P_{\beta}(\kappa'|\vec{q}) , \quad (4.44)$$

or in matrix form

$$E^{(C)} = -\frac{v_a}{e^2} CP , \quad (4.45)$$

where

$$P = \frac{e}{v_a} Zu . \quad (4.46)$$

From (4.44) we see that the elements of $C(\vec{q})$ relate the amplitude of the polarization produced by the displacements of ions of one type (κ') to the amplitude of the Coulomb field produced at another site (κ).

We now show that the total Coulomb field $E^{(C)}$ defined by (4.44) can be decomposed into three different fields whose physical meaning will be discussed below. For this purpose, we explicitly separate the term $\vec{\tau} = 0$ in the series (4.38) for $N^{(G)}(\vec{q})$. If this is done and the result is substituted in (4.36), we eventually obtain

$$C_{\alpha\beta}(\vec{q}_{KK'}) = e^2 \left[\frac{4\pi}{v_a} \frac{q_\alpha q_\beta}{q^2} - Q_{\alpha\beta}(\vec{q}_{KK'}) + \delta_{KK'} z_K^{-1} \sum_{K''} z_{K''} Q_{\alpha\beta}(0_{KK''}) \right] , \quad (4.47)$$

where

$$Q_{\alpha\beta}(\vec{q}_{KK'}) = - \frac{4\pi}{v_a} \left\{ \frac{q_\alpha q_\beta}{q^2} [\exp(-q^2/4n) - 1] + \sum_{\vec{\tau} \neq 0} \dots + \sum_{\ell'} \dots \right\} , \quad (4.48)$$

and we have not bothered to write out explicitly the sums over $\vec{\tau}$ and ℓ' in (4.48). The sum over $\vec{\tau}$ is the sum appearing in (4.38) but with $\vec{\tau} = 0$ excluded, while the sum over ℓ' is related to $N_{\alpha\beta}^{(H)}(\vec{q}_{KK'})$ defined by (4.39). As we have discussed above, the latter sum can be made negligibly small if we choose $n \gg r_0^{-2}$ in (4.33). It is important to note that as $\vec{q} \rightarrow 0$, the first term in (4.47) is not a regular function of \vec{q} because it contains q^2 in the denominator; its limiting value depends on the direction along which the point $\vec{q} = 0$ is approached. On the other hand, $Q_{\alpha\beta}(\vec{q}_{KK'})$ is a regular function as $\vec{q} \rightarrow 0$. If (4.47) is substituted in (4.44), we obtain

$$\vec{E}^{(C)} = \vec{E}^{(M)} + \vec{E}^{(L)} + \vec{E}^{(S)} . \quad (4.49)$$

In (4.49), $\vec{E}^{(M)}$ is called the *macroscopic field*, it arises from the first term in (4.47) and is given by

$$E_\alpha^{(M)}(\vec{q}_j) = - 4\pi \frac{q_\alpha}{q^2} \sum_\beta q_\beta P_\beta(\vec{q}_j) , \quad (4.50)$$

where we have introduced the polarization

$$\vec{P}(\vec{q}_j) = \sum_K \vec{P}(K|\vec{q}_j) . \quad (4.51)$$

$\vec{E}^{(M)}$ can therefore be written in the form

$$\vec{E}^{(M)} = - 4\pi \frac{(\vec{q}\vec{P})}{q^2} \vec{q} . \quad (4.52)$$

From (4.52) we see that $\vec{E}^{(M)}$ depends on the relative directions of \vec{q} and \vec{P} . If \vec{q} is perpendicular to \vec{P} , the macroscopic field vanishes, but if \vec{q} is parallel to \vec{P} , we have

$$\vec{E}^{(M)} = - 4\pi \vec{P} . \quad (4.53)$$

Since in this case $\vec{E}^{(M)}$ is opposite to \vec{P} , the field $\vec{E}^{(M)}$ is also called *de-polarization field*.

The second term in (4.49) is the *Lorentz field*; it originates from the second term in (4.47) and its α component is

$$E_{\alpha}^{(L)}(\kappa|\vec{q}) = v_a \sum_{\kappa' \beta} Q_{\alpha\beta}(\kappa\kappa') P_{\beta}(\kappa'|\vec{q}) . \quad (4.54)$$

For simple structures such as the alkali-halides and for $\vec{q} \rightarrow 0$, one obtains the familiar expression $\vec{E}^{(L)} = (4\pi/3)\vec{P}$. This will be discussed below for the case of NaCl.

Finally, the field $\vec{E}^{(S)}$ in (4.49) is the "self-field", that is, the field change at the ion at site κ owing to its own displacement; it arises from the last term in (4.47) and is given by

$$E_{\alpha}^{(S)}(\kappa|\vec{q}) = - \frac{v_a}{z_{\kappa}} \sum_{\beta} \left[\sum_{\kappa'} Q_{\alpha\beta}(\kappa\kappa') z_{\kappa'} \right] P_{\beta}(\kappa|\vec{q}) . \quad (4.55)$$

The field $\vec{E}^{(C)} - \vec{E}^{(S)}$ is the field at a lattice point due to the dipoles at all the other lattice points. For $\vec{q} \rightarrow 0$ and simple structures, the fields introduced here are discussed in many text books. KITTEL [4.34] writes $\vec{E}_{\text{local}} = \vec{E}_0 + \vec{E}_1 + \vec{E}_2 + \vec{E}_3$, where \vec{E}_0 is the external field not considered here. Comparing with our notation, we have $\vec{E}_{\text{local}} = \vec{E}_0 + \vec{E}^{(C)} - \vec{E}^{(S)}$, where $\vec{E}_1 = \vec{E}^{(M)}$ and $\vec{E}_2 + \vec{E}_3 = \vec{E}^{(L)}$. $\vec{E}^{(C)} - \vec{E}^{(S)}$ is called the *effective field* \vec{E}^* .

4.2.3 Application to Crystals with NaCl Structure

Confining ourselves to nearest-neighbour interactions for the overlap forces in the NaCl structure (Fig.4.4), we find from (4.22,23)

$$\begin{aligned} \phi_{xx}^{(R)}(12) &= - \frac{e^2}{2v_a} A = - \frac{b}{2} e^{-r_0/\rho} \\ \phi_{yy}^{(R)}(12) &= \phi_{zz}^{(R)}(12) = - \frac{e^2}{2v_a} B = \frac{b}{r_0\rho} e^{-r_0/\rho} \\ \phi_{\alpha\alpha}^{(R)}(\kappa\kappa') &= \frac{e^2}{v_a} (A + 2B) \\ \phi_{\alpha\beta}^{(R)}(\kappa\kappa') &= 0 \quad \text{for } \alpha \neq \beta . \end{aligned} \quad (4.56)$$

$\phi_{xx}^{(R)}(12)$ is a *radial force constant* (stretching of the bond formed by the ions 1 and 2), while $\phi_{yy}^{(R)}(12)$ and $\phi_{zz}^{(R)}(12)$ are *tangential force constants* (shearing

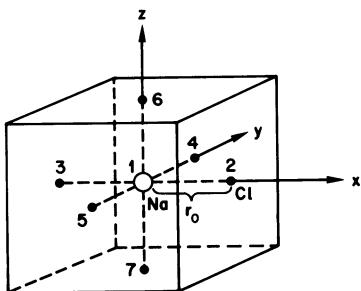


Fig. 4.4. Nearest-neighbour interactions in the NaCl structure

of the bond). Since $\rho/r_0 \approx 0.1$ [4.35], we obtain from (4.56) $B/A = \rho/r_0 \approx 0.1$. Thus, the tangential force constants are about one order of magnitude smaller than the radial force constants. From (4.56) and (4.31), the matrix elements of the repulsive matrix $R(\vec{q})$ are

$$\begin{aligned}
 R_{\alpha\alpha}(\vec{q}_{kk}) &= \frac{e^2}{v_a} (A + 2B) \\
 R_{xx}(12) &= -\frac{e^2}{v_a} (A \cos\phi_1 + B \cos\phi_2 + B \cos\phi_3) \\
 R_{yy}(12) &= -\frac{e^2}{v_a} (B \cos\phi_1 + A \cos\phi_2 + B \cos\phi_3) \\
 R_{zz}(12) &= -\frac{e^2}{v_a} (B \cos\phi_1 + B \cos\phi_2 + A \cos\phi_3) \\
 R_{\alpha\beta}(\vec{q}_{kk'}) &= 0 \quad \text{for } \alpha \neq \beta \quad ,
 \end{aligned} \tag{4.57}$$

and $\phi_\alpha = aq_\alpha/2 = r_0 q_\alpha$. Thus, the 6-dimensional matrix $R(\vec{q})$ is diagonal with respect to α and β and can be factored into three 2-dimensional matrices $R_{xx}(\vec{q})$, $R_{yy}(\vec{q})$ and $R_{zz}(\vec{q})$. From (4.36-38), it can be shown that when \vec{q} is in a special direction of high symmetry such as (100) in NaCl, the matrix $C(\vec{q})$ is also diagonal in α and β . Thus, when $\vec{q} = (q_x, 0, 0)$, one finds that the dynamical matrix $M = R + ZCZ$ has the following structure:

$$M(\vec{q}) = \begin{bmatrix} M_{xx} & & & 0 \\ & M_{yy} & & \\ 0 & & M_{zz} & \\ & & & \end{bmatrix}$$

where $M_{\alpha\alpha}(\vec{q})$ are 2-dimensional and real matrices (see the remarks at the end of Sect.3.2). In this case, the direction of the eigenvectors $\vec{e}(\kappa|\vec{j})$ are determined by symmetry and the modes are purely longitudinal or purely transverse. If $\vec{q} = (q_x, 0, 0)$, the matrix $M_{xx}(\vec{q})$ gives the dispersion $\omega(\vec{q})$ for the longitudinal modes LA and LO, while $M_{yy}(\vec{q})$ and $M_{zz}(\vec{q})$ give identical solutions for the doubly-degenerate TA and TO-modes.

It is instructive to consider the case $\vec{q} \rightarrow 0$. From (4.48), it is found for crystals such as the alkali-halides in which each ion is at a site of at least tetrahedral symmetry, that

$$Q_{\alpha\beta}(\vec{q}\rightarrow 0) = \frac{4\pi}{3V_a} \delta_{\alpha\beta} . \quad (4.58)$$

Substituting (4.58) in (4.47) and using the condition of electrical neutrality $\sum_{\kappa} z_{\kappa} = 0$, we obtain

$$C_{\alpha\beta}(\vec{q}\rightarrow 0) = e^2 \left(\frac{4\pi}{V_a} \frac{q_{\alpha} q_{\beta}}{q^2} - \frac{4\pi}{3V_a} \delta_{\alpha\beta} \right) . \quad (4.59)$$

Suppose $\vec{q} = (q_x \rightarrow 0, 0, 0)$. For this case, we obtain from (4.59)

$$C_{xx}(\vec{q}\rightarrow 0) = \frac{8\pi e^2}{3V_a} = C_L , \quad (4.60)$$

but

$$C_{yy}(\vec{q}\rightarrow 0) = C_{zz}(\vec{q}\rightarrow 0) = -\frac{4\pi e^2}{3V_a} = C_T . \quad (4.61)$$

This difference is characteristic for Coulomb interactions. It should be noted that from (4.57)

$$R_{\alpha\alpha}(\vec{q}\rightarrow 0) = R_0 = \frac{e^2}{V_a} (A + 2B) , \quad (4.62)$$

whatever the direction of \vec{q} as $\vec{q} \rightarrow 0$. From this it follows that the frequencies of LO and TO-modes, ω_{LO} and ω_{TO} , are quite different for $\vec{q} \rightarrow 0$. In fact, for $\vec{q} = (q_x \rightarrow 0, 0, 0)$, one finds from (4.57,61,62)

$$M_{xx} = (R_0 + z^2 C_L) \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} , \quad (4.63)$$

$$M_{yy} = M_{zz} = (R_0 + z^2 C_T) \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} , \quad (4.64)$$

where $z = |z_k|$. The condition $|M - m\lambda| = 0$ gives

$$\mu\omega_{L0}^2 = R_0 + \frac{8\pi z^2 e^2}{3v_a} , \quad (4.65)$$

$$\mu\omega_{T0}^2 = R_0 - \frac{4\pi z^2 e^2}{3v_a} \quad (4.66)$$

and

$$\omega_{L0}^2 - \omega_{T0}^2 = \frac{4\pi z^2 e^2}{\mu v_a} , \quad (4.67)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass. Thus we see that due to the Coulomb interaction, $\omega_{L0} > \omega_{T0}$.

We have derived this result in a purely mathematical way and it is desirable to gain some insight into its physical origin. This is possible from a consideration of the effective fields acting on the ions. First we note that as a result of (4.55,58), the field $\vec{E}^{(S)} = 0$. Secondly, from (4.54, 58) it follows that the Lorentz field is

$$\vec{E}(L) = \frac{4\pi}{3} \vec{P} . \quad (4.68)$$

The essential point is that the macroscopic field $\vec{E}^{(M)}$ is different for T0 and L0-modes. In fact from (4.52), we find that for a T0-mode (\vec{q} perpendicular to \vec{P}), the macroscopic field vanishes while for an L0-mode (\vec{q} parallel to \vec{P}), the macroscopic field is $\vec{E}^{(M)} = -4\pi\vec{P}$. Thus, the effective fields are, according to (4.49), given by

$$\vec{E}^* = \frac{4\pi}{3} \vec{P} \quad (\text{T0-mode}) , \quad (4.69)$$

$$\vec{E}^* = -\frac{8\pi}{3} \vec{P} \quad (\text{L0-mode}) . \quad (4.70)$$

It is therefore the macroscopic field which is responsible for the result $\omega_{L0} > \omega_{T0}$. Before discussing its origin, it must be emphasized that $q = 2\pi/\lambda \rightarrow 0$ implies a phonon whose wavelength is large compared with the lattice parameter a , but still small compared with the dimension d of the crystal. For smaller values of q than this, one must take explicit account of the retardation of the Coulomb interaction [4.36] and of the shape of the crystal [4.37] (see also [Ref.1.35, Chap.2]). If the condition

$$a \ll \lambda \ll d \quad (4.71)$$

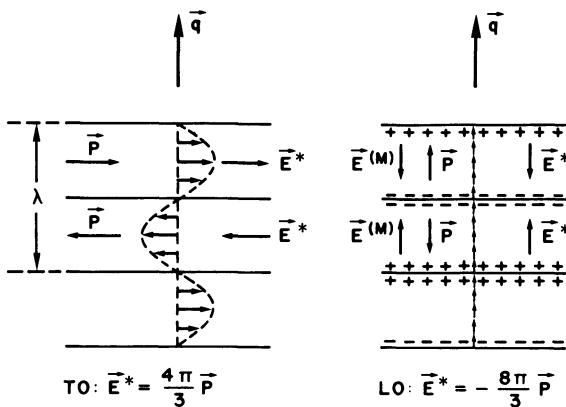


Fig. 4.5. Effective fields \vec{E}^* and polarization \vec{P} for T0 and LO-modes in the limit $\vec{q} \rightarrow 0$. The depolarization field $\vec{E}(M)$ of the LO-mode arises from an accumulation of charges in the nodal planes

is satisfied, the crystal contains many nodal planes and neighbouring nodal planes are separated by many planes of atoms (Fig.4.5). For the LO-modes, there is an accumulation of charge in the nodal planes which gives rise to the depolarization field $\vec{E}(M) = -4\pi\vec{P}$. For the T0-modes, however, there is no such accumulation of the charge and consequently, $\vec{E}(M) = 0$. As a consequence, \vec{E}^* is parallel to $\vec{P} = (ze/v_a)\vec{w}$ and tends to assist the lattice distortion $\vec{w} = \vec{u}_1 - \vec{u}_2$ associated with a T0-mode. For an LO-mode, however, \vec{E} is antiparallel to \vec{P} and tends to resist the distortion \vec{w} .

Before we can compare the phonon dispersion predicted by the rigid ion model with experiments, it is necessary to determine the parameters A and B defined by (4.22,56). The procedure is similar to the one described in Sect.4.1. The energy of the static crystal per unit cell with short-range interactions extending only to the 6 nearest-neighbour ions (Fig.4.4) is given by

$$\Phi_{uc}(r) = 6\phi^{(R)}(r) - \alpha_M \frac{(ze)^2}{r} , \quad (4.72)$$

where α_M is the *Madelung constant* referred to the nearest-neighbour separation r . α_M can also be calculated by the Ewald method described in Sect. 4.3.3 [4.38]. For NaCl, the Madelung constant is $\alpha_M = 1.7476$. At $T = 0$ and neglecting the zero-point motion (which is a very good approximation for the alkali halides), the equilibrium condition is (Sect.4.1)

$$\left[\frac{\partial \Phi_{uc}(r)}{\partial r} \right]_{r_0} = 0 , \quad (4.73)$$

where r_0 is the equilibrium distance between nearest-neighbour ions. From (4.72,73), (4.22b) and $v_a = 2r_0^3$, one finds

$$B = -\frac{2}{3} \alpha_M z^2 . \quad (4.74)$$

For NaCl ($z = 1$), one obtains $B = -1.165$. The parameter A can be obtained from the bulk modulus BM which at $T = 0$ is defined by [4.35]

$$BM = v_a \left(\frac{\partial^2 \phi_{uc}}{\partial v^2} \right) r_0 . \quad (4.75)$$

Using (4.72-74) and (4.22a), it is an easy exercise to show that

$$BM = \frac{e^2}{12r_0^4} (A + 2B) . \quad (4.76)$$

From (3.129a) and Table 3.2, we estimate for NaCl (with $r_0 \approx 2.815 \text{ \AA}$) a value of $A \approx 10.38$ which is about 9 times larger than B as mentioned at the beginning of this section.

Figure 4.6 shows the calculated values of $\omega_j(\vec{q})$ for NaI and compares them with the measured values determined by inelastic neutron scattering [4.39]. Considering the extreme simplicity of the model with only one parameter A, the agreement is surprisingly good although the longitudinal modes are generally too high, particularly for the optic branches.

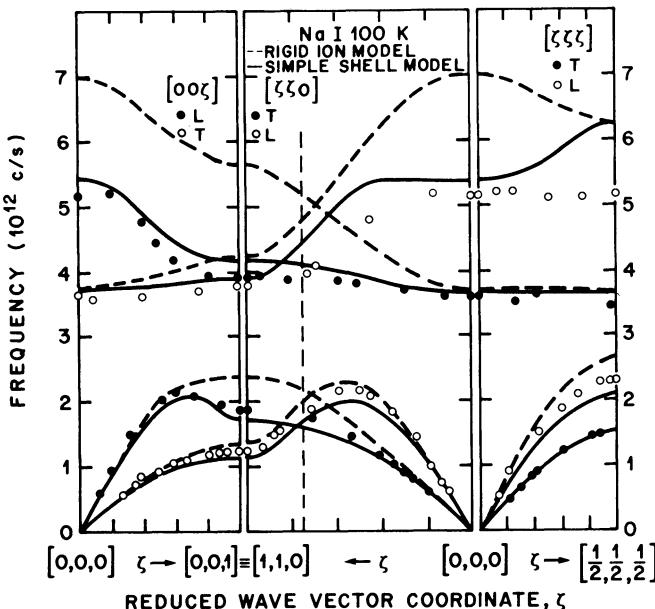


Fig.4.6. Experimental phonon frequencies for NaI for \vec{q} in each of three symmetry directions compared with calculated values based on the rigid-ion model (dotted curve) and a simple shell model (continuous curve [4.39]).

4.2.4 Deficiencies of the Rigid-Ion Model

Besides the discrepancies between calculated and observed dispersion curves as illustrated in Fig.4.5, there are other deficiencies of the rigid-ion model. Since the model is based on central forces, it predicts the Cauchy relations which for a cubic crystal are $C_{12} = C_{44}$. A glance at Table 3.2 shows that these relations are only approximately satisfied for the alkali halides.

The rigid-ion model is also inconsistent with the dielectric properties of crystals (Sect.4.3.2). At optical frequencies only the electrons (and not the ions) respond to the electric field of the light. The electronic polarization gives rise to the dielectric constant ϵ_∞ , which for the alkali halides have observed values between 2 and 3. Since the rigid-ion model ignores the electronic polarizabilities, it predicts $\epsilon_\infty = 1$.

We have represented the ionic charges by point charges. The question arises as to whether the model might be improved by replacing the point charges by rigid but extended charge distributions which appear more physically realistic. It can be shown [4.33] that if the charge distributions do not overlap, the effective field \vec{E}^* is still given by (4.69,70). This is to be expected since according to a result of elementary electrostatics, spherically symmetric charge distributions which do not overlap can be replaced by point charges. In the limit of very widely extended charge distributions, however, the Lorentz field reduces to zero, and the effective field \vec{E}^* is then equal to the macroscopic field $\vec{E}^{(M)}$ which is still given by (4.52).

4.3 The Shell Model

4.3.1 The Essential Features of the Model

The most popular model which takes into account both the ionic and electronic polarizabilities is the shell model of DICK and OVERHAUSER [4.12]. It is assumed that each ion consists of a spherical electronic shell which is isotropically coupled to its rigid ion-core by a spring. To begin with we consider a free ion which is polarized by a static field E . The spring constant is k , the displacement of the shell relative to its core is v and the charge of the shell is ye (Fig.4.7). In equilibrium, the electrostatic force yeE is equal to the elastic force kv : $yeE = kv$. The induced dipole moment is $d = yev = \alpha E$ from which we obtain the *free ion polarizability*

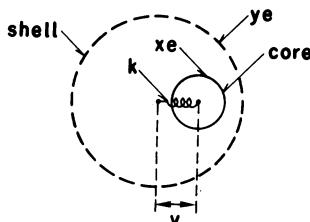


Fig.4.7. In the shell model, an ion consists of a spherical electronic shell which is isotropically coupled to its rigid ion-core by a spring with force constant k . x_e : charge of the core, y_e : charge of the shell; v is the relative displacement between core and shell

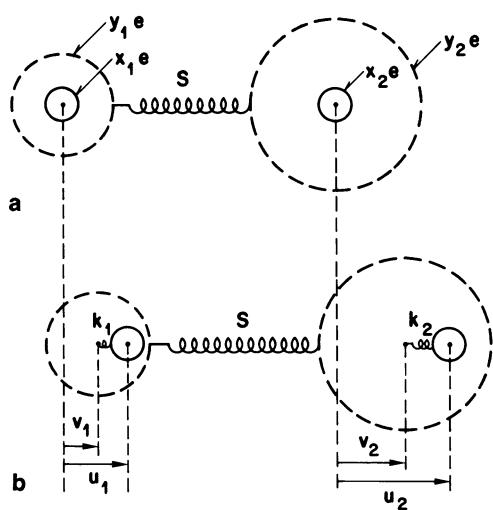


Fig.4.8a,b The coupling of two neighbouring ions in the simple shell model. a) Ions in equilibrium positions and b) ions in displaced positions, k_1 , k_2 and S are the spring constants of the model

$$\alpha = \frac{(y_e)^2}{k} . \quad (4.77)$$

We now consider a cation and a nearest-neighbour anion of a diatomic alkali halide crystal (Fig.4.8). k_1 and k_2 are the force constants which couple the shells to the ion cores. The core charges are $x_1 e$, $x_2 e$ and the shell charges are $y_1 e$, $y_2 e$. The net charge on the cation is $z_e = (x_1 + y_1)e$ and on the anion $-ze = (x_2 + y_2)e$. The short-range interionic forces are specified by a constant S acting between the shells of neighbouring ions.

Using the notation of Fig.4.8, the equations of motion for a T0-mode at $\vec{q} = 0$ are

$$m_1 \ddot{u}_1 = k_1(v_1 - u_1) + x_1 e E^* , \quad (4.78)$$

$$m_2 \ddot{u}_2 = k_2(v_2 - u_2) + x_2 e E^* , \quad (4.79)$$

$$0 = S(v_2 - v_1) + k_1(u_1 - v_1) + y_1 e E^* , \quad (4.80)$$

$$0 = S(v_1 - v_2) + k_2(u_2 - v_2) + y_2 e E^* . \quad (4.81)$$

Here, m_1 and m_2 are the masses of the cores and E^* is the effective field. The masses of the shells have been taken to be zero which is equivalent

to the adiabatic approximation discussed in Chap.1. Elimination of the shell coordinates v_1 and v_2 leads, after some elementary calculations, to

$$\mu \ddot{w} + S^* w = z^* e E^* , \quad (4.82)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$, $w = u_1 - u_2$ and

$$S^* = \frac{k_1 k_2 S}{k_1 k_2 + (k_1 + k_2) S} , \quad (4.83)$$

$$z^* = z + \frac{\frac{y_2}{k_2} - \frac{y_1}{k_1}}{\frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{S}} . \quad (4.84)$$

In the absence of an external field, the effective field E^* is given by (4.69,70) and we write

$$E^* = \beta P , \quad (4.85)$$

where $\beta = 4\pi/3$ for T0-modes and $\beta = -8\pi/3$ for L0-modes in alkali halides. Further, it is evident that the polarization is given by

$$P = \frac{e}{v_a} (x_1 u_1 + x_2 u_2 + y_1 v_1 + y_2 v_2) . \quad (4.86)$$

Eliminating v_1 and v_2 again with the help of (4.80,81), we obtain

$$P = \frac{1}{v_a} (z^* e w + \alpha^* E^*) , \quad (4.87)$$

where

$$\frac{\alpha^*}{e^2} = \frac{y_1^2}{k_1} + \frac{y_2^2}{k_2} - \frac{\left(\frac{y_1}{k_1} - \frac{y_2}{k_2}\right)^2}{\frac{1}{S} + \frac{1}{k_1} + \frac{1}{k_2}} . \quad (4.88)$$

From (4.85,87), it follows that

$$E^* = k \beta \frac{z^* e}{v_a} w , \quad (4.89)$$

where

$$k = \left(1 - \beta \frac{\alpha^*}{v_a}\right)^{-1} . \quad (4.90)$$

Substituting (4.89) in (4.82) and putting $w = w_0 \exp(-i\omega t)$, we obtain for the frequencies of the T0 and L0-modes

$$\mu\omega_{T0}^2 = S^* - \frac{4\pi(z^*e)^2}{3v_a} k_T , \quad (4.91)$$

$$\mu\omega_{L0}^2 = S^* + \frac{8\pi(z^*e)^2}{3v_a} k_L , \quad (4.92)$$

where

$$k_T = \left(1 - \frac{4\pi\alpha^*}{3v_a}\right)^{-1} \quad (4.93)$$

and

$$k_L = \left(1 - \frac{8\pi\alpha^*}{3v_a}\right)^{-1} . \quad (4.94)$$

The most important implications of the shell model are:

a) If k_1 and k_2 are made infinite we obtain $S^* = S$, $z^* = z$, $\alpha^* = 0$ and $k_T = k_L = 1$; the relations (4.91,92) then reduce to the relations (4.65,66) for the rigid-ion model as would be expected.

b) The electronic polarizability per ion pair is not just the sum of the free ion polarizabilities which, according to (4.77), is $\alpha = \alpha_1 + \alpha_2 = (y_1 e)^2/k_1 + (y_2 e)^2/k_2$. The presence of the third term in (4.88) leads to $\alpha^* < \alpha$.

c) The effective or dynamic charge z^*e is different from the formal charge ze . Since the anion is usually more polarizable than the cation, the second term in (4.84) is negative with the result that $z^*e < ze$. This result has already been obtained by SZIGETI but without using the language of the shell model [4.40]. The dynamic charge z^*e is, therefore, also known as the *Szigeti charge* e_s^* . Szigeti charges of a number of diatomic crystals are given in [1.35].

d) The effective charge is not, in general, zero even if there is no ionicity, i.e., if $z = 0$, z^* is not zero. Examples are III - V compounds like InSb and GaAs; there is reason to believe that these compounds are largely covalent, that is, $ze \approx 0$, but nevertheless, they show strong one-phonon infrared absorption which, in the case of GaAs, is due to an effective charge z^*e as large as 0.51 e [4.41]. On the infrared evidence alone one cannot, therefore, arrive at a clear separation of the two contributions to z^*e given by (4.84). Our simple model predicts that for neutral and identical atoms, $z^*e = 0$ (in this case $z = 0$ and $y_1/k_1 = y_2/k_2$). This is true, for instance, for the carbon atoms in diamond; here $z^*e = 0$ and correspondingly, no one-phonon infrared absorption is observed [1.35]. However, the

same carbon atoms in graphite do have small effective charges $z^* e \neq 0$ which give rise to weak one-phonon infrared absorption [4.42]. The existence of nonvanishing dynamical charges $z^* e$ is, therefore, closely related to the symmetry and structure of the crystal, and a shell model which takes these features into account does indeed yield $z^* e \neq 0$ for crystals such as graphite or Te.

4.3.2 The Dielectric Constant and the Lyddane-Sachs-Teller Relation

The dielectric constant $\epsilon(\omega)$ of a crystal is found by considering the equations of motion in a transverse electric field $E = E_0 \exp[i(\vec{k}\vec{r} - \omega t)]$ applied from outside the crystal and for which $\vec{k} \rightarrow 0$. For frequencies in the infrared and far-infrared regions, such fields can excite T₀-modes at $\vec{q} \rightarrow 0$ [1.35]. The equation of motion and the polarization are given by (4.82,87) but the effective field now includes the external field as well, that is,

$$E^* = E + \frac{4\pi}{3} P . \quad (4.95)$$

From (4.87,95), it follows that

$$E^* = k_T \left(E + \frac{4\pi z^* e}{3V_a} w \right) \quad (4.96)$$

and

$$P = \frac{k_T}{V_a} (\alpha^* E + z^* e w) . \quad (4.97)$$

Substituting (4.96) in (4.82) and using (4.91) gives

$$w(\omega) = \frac{k_T z^* e E}{\mu(\omega_{T0}^2 - \omega^2)} . \quad (4.98)$$

$w(\omega)$ describes the response of the crystal to the external field E ; it represents a forced oscillation with a singularity at $\omega = \omega_{T0}$. We should, of course, introduce a damping into the equation of motion; this would limit the amplitude w to a finite value at $\omega = \omega_{T0}$ (Chap.5). The electric displacement is defined by

$$D = \epsilon E = E + 4\pi P , \quad (4.99)$$

from which we obtain the dielectric constant

$$\epsilon = 1 + 4\pi P/E . \quad (4.100)$$

From this equation, together with (4.97,98) we obtain

$$\epsilon(\omega) = 1 + \frac{4\pi\alpha^*}{v_a} k_T + \frac{4\pi(z^* e)^2 k_T^2}{\mu v_a (\omega_{T0}^2 - \omega^2)} . \quad (4.101)$$

For $\omega \gg \omega_{T0}$ only the electrons (and not the ions) can respond to the external field E and we obtain for the high frequency dielectric constant

$$\epsilon_\infty = 1 + \frac{4\pi\alpha^*}{v_a} k_T . \quad (4.102)$$

ϵ_∞ is the dielectric constant at frequencies well above the phonon frequencies but below the electronic excitation frequencies.

Using (4.93) and solving (4.102) for $4\pi\alpha^*/3v_a$, we obtain the relation of Clausius-Mosotti

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi\alpha^*}{3v_a} . \quad (4.103)$$

From (4.102,103), it follows that

$$k_T = \frac{\epsilon_\infty + 2}{3} . \quad (4.104)$$

Substituting (4.102,104) in (4.101) yields

$$\epsilon(\omega) = \epsilon_\infty + \frac{4\pi(z^* e)^2}{\mu v_a (\omega_{T0}^2 - \omega^2)} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 . \quad (4.105)$$

At this point, it is convenient to introduce the *transverse effective charge* e_T^* defined by

$$e_T^* = \frac{\epsilon_\infty + 2}{3} z^* e . \quad (4.106)$$

Introducing e_T^* in (4.91,92) and using (4.104) gives

$$\mu \omega_{T0}^2 = S^* - \frac{4\pi e_T^{*2}}{v_a (\epsilon_\infty + 2)} , \quad (4.107)$$

$$\mu \omega_{L0}^2 = S^* + \frac{8\pi e_T^{*2}}{v_a \epsilon_\infty (\epsilon_\infty + 2)} , \quad (4.108)$$

from which we obtain

$$\omega_{L0}^2 - \omega_{T0}^2 = \frac{4\pi e_T^{*2}}{\mu v_a \epsilon_\infty} . \quad (4.109)$$

Equation (4.105) can be written in the form

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{4\pi e_T^{*2}}{\mu v_a (\omega_{T0}^2 - \omega^2)} \quad (4.110)$$

and the polarization and effective field assume the following form:

$$P = \frac{1}{v_a} e_T^{*2} w + \frac{\epsilon_{\infty} - 1}{4\pi} E \quad , \quad (4.111)$$

$$E^* = \frac{4\pi}{v_a} e_T^{*2} w + \frac{\epsilon_{\infty} + 2}{3} E \quad . \quad (4.112)$$

Putting $\omega = 0$ in (4.110), we obtain the static dielectric constant

$$\epsilon_0 = \epsilon_{\infty} + \frac{4\pi e_T^{*2}}{\mu v_a \omega_{T0}^2} \quad , \quad (4.113)$$

and together with (4.109), the important *relation of Lyddane-Sachs and Teller* (LST) is obtained:

$$\frac{\epsilon_0}{\epsilon_{\infty}} = \frac{\omega_{L0}^2}{\omega_{T0}^2} \quad . \quad (4.114)$$

It should be emphasized that this relation has originally been derived without making any specific assumptions about the nature of the forces between the ions [4.43]. The limits of the validity of the LST relation at long wavelengths due to retardation effects are discussed [Ref.1.35, in Chap.2]. Figure 4.9 displays $\epsilon(\omega)$. Note that $\epsilon(\omega_{L0}) = 0$. For the rigid ion model $\epsilon_{\infty} = 1$. The parameters ω_{T0} , ϵ_{∞} , ϵ_0 and e_T can be determined from reflectivity and transmission measurements in the infrared [1.35]. Values of these parameters for a number of selected compounds are given in [1.35].

The relation (4.110) for $\epsilon(\omega)$ applies for optically isotropic diatomic crystals with one L0-mode and two degenerate T0-modes at $\vec{q} \approx 0$. Crystals of the same symmetry containing n ions in the unit cell possess $n - 1$ longitudinal optical modes with frequencies $\omega_j(L0)$ and $n - 1$ doubly degenerate transverse optical modes with frequencies $\omega_j(T0)$, and the generalized expression for $\epsilon(\omega)$ is

$$\epsilon(\omega) = \epsilon_{\infty} + \sum_j \frac{s_j}{\omega_j^2(T0) - \omega^2} \quad , \quad (4.115)$$

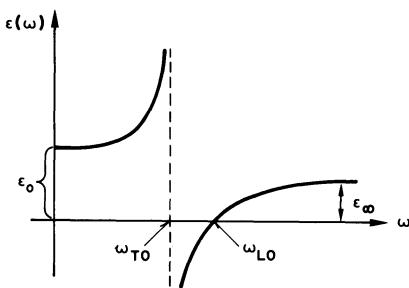


Fig. 4.9. Plot of the dielectric constant $\epsilon(\omega)$ according to (4.110)

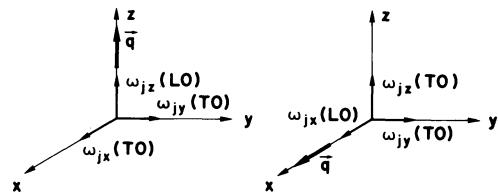


Fig. 4.10. T0 and L0-modes for a uniaxial crystal for \vec{q} parallel and perpendicular to the optical axis

where S_j is the oscillator strength of mode j which depends on the eigenvector, the effective charges and the masses (see Problem 5.6). From this it follows (Problem 4.8.3) that the generalization of the LST relation (4.114) is [4.44]

$$\frac{\epsilon_0}{\epsilon} = \pi \sum_j \frac{\omega_j^2(L0)}{\omega_j^2(T0)} . \quad (4.116)$$

A further generalization of (4.115,116) which applies to crystals of arbitrary symmetry has been derived by COCHRAN and COWLEY [4.45]. As an example, we give the result for the LST relation for a uniaxial crystal whose optical axis is the z-axis (Fig.4.10). If $\vec{q} \approx 0$ is parallel to the z-axis, there are $n - 1$ L0-modes with frequencies $\omega_{jz}(L0)$ and $n - 1$ doubly-degenerate T0-modes with frequencies $\omega_{jx}(T0) = \omega_{jy}(T0)$. However, if $\vec{q} \approx 0$ is parallel to the x-axis, there are $n - 1$ L0-modes with frequencies $\omega_{jx}(L0)$, $n - 1$ T0-modes with frequencies $\omega_{jy}(T0)$ and $n - 1$ T0-modes with frequencies $\omega_{jz}(T0)$. Note that in the latter case, the degeneracy of the modes polarized perpendicular to the z-axis is lifted, that is, $\omega_{jx}(L0) \neq \omega_{jy}(T0)$; this is a consequence of the macroscopic field (4.52) which is associated with the L0-modes but which is absent for the T0-modes. The LST relation for a uniaxial crystal is

$$\pi \sum_j \frac{\omega_{j\alpha}(L0)}{\omega_{j\alpha}(T0)} = \frac{\epsilon_\alpha(0)}{\epsilon_\alpha(\infty)} , \quad (4.117)$$

where $\epsilon_\alpha(0)$ and $\epsilon_\alpha(\infty)$ are the static and high frequency dielectric constants measured in the direction α .

4.3.3 Generalized Shell Model and Phonon Dispersions

Among the most interesting and successful applications of the shell model has been its use in calculating $\omega(\vec{q})$ dispersion relations. For this purpose, COCHRAN [4.10,11,13,14] introduced a generalization of the shell model which, to use the picture developed in Sect.4.3.1, introduces additional interactions between the cores of the ions and between the core of one ion and the shell of another (Fig.4.11).

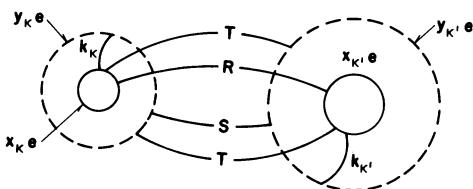


Fig.4.11. The generalized shell model of COCHRAN illustrating the different interactions between two neighbouring ions κ and κ'

We give the result without derivation. The dynamical matrix $M(\vec{q})$ can be written in the form

$$M = R + ZCZ - (T + ZCY)(S + YCY)^{-1}(T^+ + YCZ) \quad . \quad (4.118)$$

In this expression, $R + ZCZ$ describes the interaction between rigid ions, see (4.29). C is the Coulomb matrix discussed in Sects.4.2.1,2. The third term in (4.118) takes into account the polarizability of the ions. T includes the intra-ionic core-shell interactions k . Z and Y are diagonal $3n \times 3n$ matrices which designate the ion charges $z_k e$ ($z_k = x_k + y_k$) and the shell charges $y_k e$, respectively. The terms ZCZ , ZCY and YCY describe the electrostatic core-core, core-shell and shell-shell interactions, respectively. On the basis of this model, dispersion curves have been calculated for a number of crystals; an example is shown for NaI in Fig.4.6 where the following simplifying assumptions have been made [4.39]: (i) short-range forces extend only to nearest neighbours and the forces are central, (ii) only the negative ion is polarizable, (iii) the short-range interaction S is between the positive ion and the shell of the negative ion and not the core, and (iv) the ionic charges are $\pm e$. The theory then involves three parameters, namely, k , y and S which were chosen to agree with the macroscopic quantities C_{11} , ϵ_0 and ϵ_∞ . The extent of the agreement is shown by the full lines in Fig.4.6. The agreement is considerably better than for the rigid-ion model but discrepancies remain, particularly for the LO-modes with $\vec{q} = (1/2, 1/2, 1/2)$.

A more general shell model in which some of the above restrictions have been relaxed has subsequently been applied to NaI [4.39]. Good agreement with experiments is achieved but the model does contain nine parameters.

An interesting extension of the shell model is the *deformable shell model* or breathing shell model introduced by SCHRÖDER [4.16]. This model allows for radial deformations of the shells in the course of lattice vibrations which leads to three-body interactions and, correspondingly, the model does not predict the Cauchy relations [4.46].

It should also be mentioned that other lattice dynamical model exist which, in many respects, are equivalent to the shell model; an important one is the *deformation dipole model* put forward by HARDY [4.47].

When the ionic charges are set equal to zero ($z = 0$), we obtain from (4.118)

$$M = R - T(S + YCY)^{-1}T^+ . \quad (4.119)$$

Thus, the dynamical matrix still depends on the electronic polarizabilities of the atoms. Even in the absence of Coulomb interactions ($C = 0$), the dynamical matrix

$$M = R - TS^{-1}T^+ \quad (4.120)$$

is still influenced by the deformability of the atoms. Equation (4.119) has been applied to covalent crystals although it clearly lacks intuitive appeal when applied to a material with strongly covalent bonds such as Si or Ge. The applicability of the model to such crystals is partly justified by its success although it should be remembered that the assumptions on which (4.119) are derived are only those of the dipole approximation. The results of the shell model for Ge are shown in Fig.4.12 [4.10]. The model contains 5 parameters, two of which are determined from the elastic constants while the three remaining parameters were chosen to fit ϵ_∞ and to give overall agreement with the measured $\omega_j(\vec{q})$. Figure 4.12 shows that the model is able to describe the major factors which determine the lattice dynamics of Ge.

In the above discussion of the shell-model, we have assumed that the atoms or ions are not statically polarized. This is only the case for structures with sufficiently high symmetry. However, in general structures, the ions are often located at sites with low symmetry and therefore carry static induced electronic dipoles. Examples are layer structures such as PbI_2 . Because of the large polarizabilities of the nonmetals, we expect that their electric static dipole moments are important for the understanding of static and dynamic properties of these layer compounds. An extended shell model for

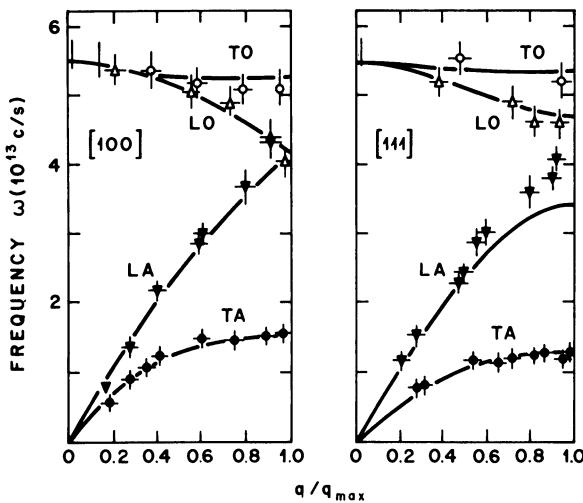


Fig.4.12. Phonon dispersion of Ge. The calculated branches (solid lines) are based on a shell model (4.119) which contains 5 parameters [4.10]

layer compounds which includes both static and dynamically induced electrostatic dipole moments has been applied to PbI_2 , CdI_2 , SnS_2 , and SnSe_2 [4.48,49]. It has indeed been shown that the static dipole moments have a very large effect on the vibrational frequencies.

4.4 The Adiabatic Bond Charge Model

The phonon dispersion curves of all covalent semiconductors with diamond or sphalerite structure show one characteristic feature from which only diamond itself is an exception: the TA phonon branches have very low frequencies and are very flat away from the zone center, although the corresponding shear moduli (slopes of $\omega(\vec{q})$ at $\vec{q} = 0$) have rather high values. Examples of dispersion curves for Ge and GaAs are shown in Figs.4.13,14. This behaviour is most easily understood with the bond charge model which has been developed for the lattice dynamics of covalent materials.

The covalent bond is usually formed from two electrons, one from each atom participating in the bond. These electrons tend to be partially localized in the region between the two atoms and constitute the *bond charge* (BC). If each "ion" contributes a charge $-Ze/2$ to each bond of a tetrahedrally coordinated compound, the magnitude of the BC is $-Ze$ and the "ions"

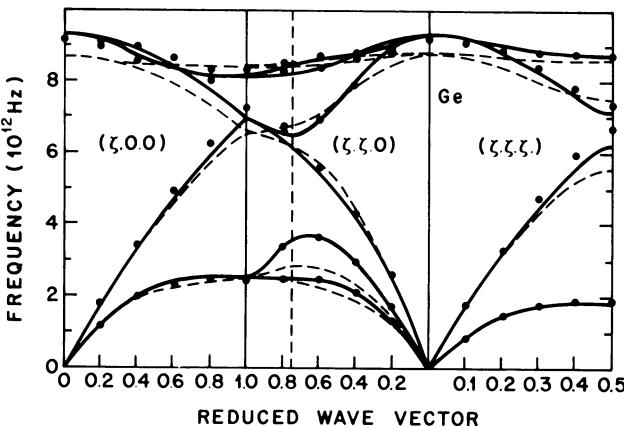


Fig. 4.13. Phonon dispersion of Ge. The calculated frequencies (solid lines) are based on the bond charge model (4.127) containing 4 parameters only [4.17]. Dashed lines depict the results from the shell model of [4.10]

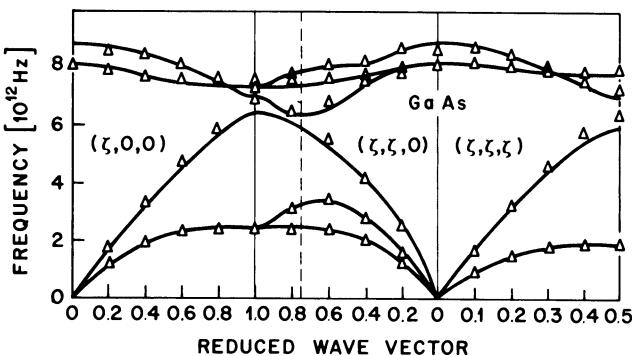


Fig. 4.14. Phonon dispersion of GaAs. The calculated frequencies (solid lines) are based on the bond charge model (4.127) containing 6 parameters [4.18]

carry a charge of $+2Ze$ (Fig. 4.15). In the monoatomic compounds Si, Ge, and C, the equilibrium sites of the BC are midway between the atoms. In heteropolar A^3B^5 semiconductors, the BC is believed to shift toward the group V ion and divides the bond length roughly in the ratio 5:3 [4.50].

In the bond charge model, the effect of the metal-like binding is described by central forces between nearest-neighbour ions while the covalent bonding is described by interactions involving the BC's [4.51,52]. In the adiabatic bond charge model of WEBER [4.17,18], the constraint that the BC's are fixed on the midway positions between the atoms is removed. Instead, they are allowed to move adiabatically like the electronic shells in the shell

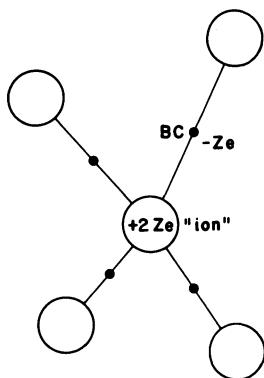


Fig.4.15. Charge distribution of the bond charge model in a tetrahedrally coordinated compound. Each "ion" carries a charge $+2Ze$ while the bond charge (BC) is $-Ze$

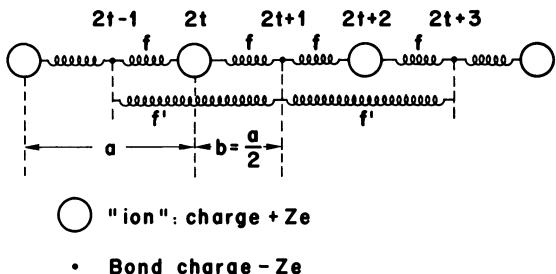


Fig.4.16. Linear chain formed by alternating ions and bond charges. F and f' are the force constants of the model

model. In order to stabilize the BC's in their sites, short-range ion-BC forces are introduced. In addition, a coupling between nearest BC's is considered. Besides these short-range forces, the Coulomb interactions between the BC's and the ions are taken into account.

To illustrate the essential ideas, we consider a monoatomic linear chain with BC's midway between the ions (Fig.4.16) [4.17]. We introduce a short-range ion-BC force constant f and a force constant f' which describes the coupling between nearest BC's. For the sake of simplicity, the short-range interaction between neighbouring ions as well as the Coulomb interactions are neglected. The equations of motion are (u : coordinates of the ions, v : coordinates of the BC's)

$$\begin{aligned} m\ddot{u}_{2t} &= f(v_{2t+1} + v_{2t-1} - 2u_{2t}) , \\ m_{BC}\ddot{v}_{2t+1} &= 0 = f(u_{2t+2} + u_{2t} - 2v_{2t+1}) \\ &\quad + f'(v_{2t+3} + v_{2t-1} - 2v_{2t+1}) . \end{aligned} \quad (4.121)$$

We have put $m_{BC} = 0$ which is equivalent to the adiabatic approximation. With the Ansatz

$$\begin{aligned} u_{2t} &= ne^{i(2tbq-\omega t)} , \\ v_{2t+1} &= \xi e^{i[(2t+1)bq-\omega t]} , \end{aligned} \quad (4.122)$$

one obtains

$$m\omega^2 \eta = 2f(\eta - \xi \cos qb) , \quad (4.123a)$$

$$f(\eta \cos qb - \xi) + f' \xi (\cos 2qb - 1) = 0 , \quad (4.123b)$$

from which it follows that the amplitude ξ of the BC's is given by

$$\xi = \frac{f \cos(qb)}{f + 2f' \sin^2(qb)} \cdot \eta . \quad (4.124)$$

Substituting (4.124) in (4.123a) gives

$$m\omega^2(q) = 2f \frac{(f + 2f') \sin^2(\frac{1}{2}aq)}{f + 2f' \sin^2(\frac{1}{2}aq)} . \quad (4.125)$$

For $q \ll \pi/a$, we obtain from (4.125)

$$\omega^2(q) = \frac{a^2}{2m} (f + 2f') q^2 = v^2 q^2 = \frac{C}{\rho} q^2 \quad (4.126)$$

and we see that the elastic constant $C \sim f + 2f'$. Figure 4.17 shows $\omega(q)$ calculated according to (4.125); in this figure, the elastic constant is the same for all curves but the ratio f'/f is different. Thus, $f \sim C/(1 + 2f'/f)$ and therefore f decreases with increasing f'/f . If $f'/f \gg 1$, one obtains the typical flattening of $\omega(q)$ away from $q = 0$. In this case, the ions are coupled only weakly to the BC's, which form an almost rigid lattice. The ions oscillate like Einstein oscillators in the lattice of the BC's and their frequency is given by the weak ion-BC force constant f . However, in the long-wavelength limit, the strong bond-bond interaction described by f' determines the frequency as can be seen from (4.126), and this produces the high value of the elastic constant.

We quote without proof the equations of motion for the general three-dimensional case [4.17]:

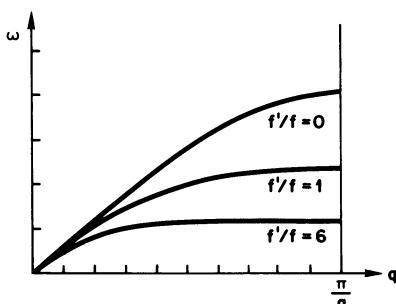


Fig. 4.17. Dispersion curves for a monoatomic linear chain with adiabatically moving bond charges, calculated according to (4.125)

$$m\omega^2 u = \left[R + 4 \frac{(ze)^2}{\epsilon} C_R \right] u + \left[T - 2 \frac{(ze)^2}{\epsilon} C_T \right] v , \\ 0 = \left[T^+ - 2 \frac{(ze)^2}{\epsilon} C_T^+ \right] u + \left[S + \frac{(ze)^2}{\epsilon} C_S \right] v . \quad (4.127)$$

Here, m , ze , and ϵ are the ion mass, the value of the BC and the dielectric constant, respectively. u and v are the vectors formed by the displacement coordinates of the ions and the BC's, respectively. R , T , and S are the dynamical matrices of the short-range ion-ion, ion-BC and BC-BC interactions. C_R , C_T , and C_S denote the corresponding Coulomb matrices which can be evaluated by the Ewald method described in Sect.4.2.2. As the band structure of Si and Ge is nearly-free-electron-like, the Coulomb interactions are screened by the factor $1/\epsilon$. Figures 4.13,14 show the results of the calculations for Ge and for GaAs. The agreement with experiments is excellent with only four parameters for Ge and six parameters for GaAs. Note that with the four parameters of the BC model, a better agreement with experiments is obtained than with the five parameters of the shell model in the case of Ge (Figs.4.12,13).

An adiabatic bond charge model for covalent crystals has also been put forward by JOHNSON [4.53] and by JOHNSON and MOORE [4.54]; in contrast to WEBER's model, all interactions in Johnsons model are purely electrostatic. Finally, it should be mentioned that bond charge models have also been used to study the vibrations of diatomic and polyatomic molecules [4.55,56].

4.5 The Valence Force Model

We now turn to a consideration of the valence force model. This model has been widely used in analyzing molecular vibrations [4.19,20] but has been extended to study phonons in covalent or partly covalent crystals [4.21,22]. To illustrate the valence force field, we first consider the H_2O molecule (Fig.4.18). The valence coordinates are bond distance changes and interbond angle changes. For the H_2O molecule, we define three internal coordinates r_t , where $r_1 = \Delta r_{31}$ and $r_2 = \Delta r_{32}$ are the changes of the bond distances r_{31} and r_{32} , and $r_3 = \sqrt{r_{31}r_{32}}\Delta\alpha$; $\Delta\alpha$ is the change of the bond angle α and the factor $\sqrt{r_{31}r_{32}}$ is introduced for convenience. In the harmonic approximation, the potential energy is written in the form

$$2\Phi = \sum_{tt'} F_{tt'} r_t r_{t'} , \quad (4.128)$$

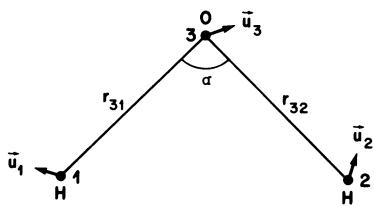


Fig. 4.18. Internal coordinates Δr_{31} , Δr_{32} and $\Delta\alpha$ of the water molecule

where F_{tt} are the force constants. For the potential energy of the H_2O molecule ($r_{31} = r_{32} = r$), we write

$$2\Phi = F_r(\Delta r_{31}^2 + \Delta r_{32}^2) + F_\alpha(r\Delta\alpha)^2 + F_{rr}(\Delta r_{31}\Delta r_{32} + \Delta r_{32}\Delta r_{31}) + F_{r\alpha}[\Delta r_{31}(r\Delta\alpha) + \Delta r_{32}(r\Delta\alpha)] .$$

It is often possible to obtain a reasonable first approximation by neglecting the cross terms associated with $\Delta r_{31}\Delta r_{32}$, $\Delta r_{31}(r\Delta\alpha)$, etc., because the force constants F_{rr} , $F_{r\alpha}$ are usually considerably smaller than the diagonal elements F_r and F_α of the F -matrix. Furthermore, F_r is roughly ten times smaller than F_α . For the H_2O molecule, $F_r = 7.8$ mdyn/ \AA and $F_\alpha = 0.69$ mdyn/ \AA (1 mdyn = 10^{-3} dyn, 1 dyn = 1 gr cm s^{-2}). Extensive tables exist for the force constants of a large number of molecules and the reader is referred to the literature [4.19,20].

Since the internal coordinates r_t represent changes of distances and angles, they are unaltered by pure translations or rotations of the molecule. Therefore, the potential energy is automatically invariant to those motions. Another advantage of the valence force field is that it is often possible to transfer force constants from one molecule to another molecule or crystal which contain similar bonds.

For molecular vibrations there is a well-established technique called the GF technique, which was developed by WILSON et al. [4.19]. An internal coordinate r_t can always be expressed in terms of the components of the Cartesian displacement coordinates $u_{\kappa\alpha}$ of the molecule ($\kappa = 1, 2, \dots, N$; $\alpha = x, y, z$):

$$r_t = \sum_{\kappa\alpha} B_{t,\kappa\alpha} u_{\kappa\alpha} . \quad (4.129)$$

In Appendix L, the coefficients $B_{t,\kappa\alpha}$ are given for stretching coordinates (Δr) and bending coordinates ($\Delta\alpha$). In [4.19], it is shown that in terms of the coordinates r_t , the kinetic energy is given by

$$2T = \sum_{tt'} (G^{-1})_{tt'} \dot{r}_t \dot{r}_{t'} , \quad (4.130)$$

where

$$G_{tt'} = \sum_{\kappa\alpha} m_{\kappa}^{-1} B_{t,\kappa\alpha} B_{t',\kappa\alpha} , \quad (4.131)$$

and the eigenvalues $\lambda_k = \omega_k^2$ are obtained from the secular equation

$$|GF - \lambda E| = 0 . \quad (4.132)$$

It is possible to extend this method to crystals and the reader is referred to the excellent book by DECIUS and HEXTTER [4.22]. An alternative approach consists of expressing the potential energy directly in terms of Cartesian displacement coordinates [4.21]. The expression (4.128) generalized for crystals can be written in the form

$$2\Phi = N \sum_{\ell} r^T(0) F_{0,\ell} r(\ell) . \quad (4.133)$$

In (4.133), the sum extends over all N cells of the crystal. $r(\ell)$ is a column vector containing as elements the valence coordinates $r_t(\ell)$ of cell ℓ . Each $F_{0,\ell}$ is a square force constant matrix in which the elements are the force constants expressing the interaction between the coordinates in cells 0 and ℓ . The generalization of (4.129) is

$$r(\ell) = \sum_m B_{\ell,m} u(m) , \quad (4.134)$$

where $u(m)$ denotes a $3n$ -dimensional column vector containing as elements the displacement coordinates $u_{\alpha\kappa}^{(m)}$ of cell m . Each $B_{\ell,m}$ is a matrix which tells how the internal coordinates are altered by the displacements in cell m ; the elements of the matrices $B_{\ell,m}$ are identical to the coefficients appearing in (4.129) (Appendix L). We show in the Appendix L that the potential energy is given by

$$2\Phi = \sum_{\vec{q}} U^+(\vec{q}) M(\vec{q}) U(\vec{q}) , \quad (4.135)$$

where

$$U(\vec{q}) = \frac{1}{\sqrt{N}} \sum_m u(m) e^{i\vec{q}\vec{r}(m)} \quad (4.136)$$

and

$$M(\vec{q}) = B^+(\vec{q}) F(\vec{q}) B(\vec{q}) . \quad (4.137)$$

The matrix

$$B(\vec{q}) = \sum_{\ell} B_{0,\ell} e^{-i\vec{q}\vec{r}(\ell)} \quad (4.138)$$

is a rectangular matrix of dimension $s \times 3n$, where s is the number of internal coordinates and n the number of atoms per unit cell. $F(\vec{q})$ is a square matrix of dimension s given by

$$F(\vec{q}) = \sum_{\ell} F_{0,\ell} e^{-i\vec{q}\cdot\vec{r}(\ell)} . \quad (4.139)$$

The eigenvalues are obtained from the secular equation

$$|M(\vec{q}) - m\omega^2(\vec{q})| = 0 , \quad (4.140)$$

where m is a diagonal matrix containing the masses.

The internal coordinates associated with a primitive unit cell must be chosen according to the following rules:

- a) each cell ℓ contains the same set of internal coordinates $r_t(\ell)$;
- b) each $r_t(\ell)$ belongs to one and only one cell ℓ .

We illustrate the procedure by considering the one-dimensional conductor $(SN)_x$ which consists of parallel zig-zag chains '...'SNSN'...' [4.57] (Fig.4.19). In order to simplify, we consider only the in-plane vibrations of a single chain. According to (4.133), we make the following Ansatz for the potential energy per unit cell:

$$\begin{aligned} 2\Phi/N &= r^T(0)F_{0,0}r(0) = \sum_t F_t r_t^2(0) \\ &= F_1 \Delta r_1^2 + F_2 \Delta r_2^2 + F_3 r_1 r_2 \Delta \alpha_1^2 + F_4 r_1 r_2 \Delta \alpha_2^2 . \end{aligned} \quad (4.141)$$

In writing (4.141), we have neglected all cross terms, that is, all interactions of the form $r_t(0)r_{t'}(\ell)$. In this approximation, $F(q)$ given by (4.139) is a diagonal matrix and independent of q :

$$F(q) = F_{0,0} = \begin{bmatrix} F_1 & & & \\ & F_2 & & 0 \\ 0 & & F_3 & \\ & & & F_4 \end{bmatrix}$$

and the transformation (4.134) reads

$$r(0) = B_{0,0}u(0) + B_{0,1}u(1)$$

or explicitly,

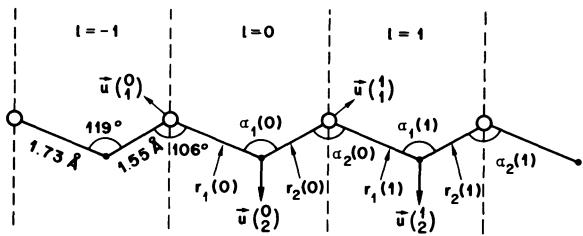


Fig.4.19. Internal coordinates of a chain of the one-dimensional conductor $(SN)_x$

$$\begin{bmatrix} \Delta r_1 \\ \Delta r_2 \\ \sqrt{r_1 r_2} \Delta \alpha_1 \\ \sqrt{r_1 r_2} \Delta \alpha_2 \end{bmatrix} = \begin{bmatrix} x & x & x & x \\ 0 & 0 & x & x \\ x & x & x & x \\ 0 & 0 & x & x \end{bmatrix} \begin{bmatrix} u_x(0)_1 \\ u_y(0)_1 \\ u_x(0)_2 \\ u_y(0)_2 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 & 0 \\ x & x & 0 & 0 \\ x & x & 0 & 0 \\ x & x & x & x \end{bmatrix} \begin{bmatrix} u_x(1)_1 \\ u_y(1)_1 \\ u_x(1)_2 \\ u_y(1)_2 \end{bmatrix}$$

The crosses in the matrices $B_{0,0}$ and $B_{0,1}$ indicate the nonzero elements which can be obtained from Appendix L. The structure of these matrices follows immediately from Fig.4.19. The matrix $B(q)$ of (4.138) is given by

$$B(q) = B_{0,0} + B_{0,1} e^{-iqa} .$$

The valence force model has been applied to diamond. Bond stretching and bond bending coordinates are introduced and the model involves 6 independent force constants (one stretching, one bending and 4 interaction constants). These 6 parameters were fitted to the observed phonon spectrum of diamond with the results shown in Fig.4.20, where it may be noted that a good fit has been achieved.

The valence force model can also be extended to apply to mixed ionic-covalent crystals. The dynamical matrix then consists of two parts, one which describes the short-range valence forces and is given by (4.135), and the other which takes into account the long-range dipole interactions of the polarizable ions. The "valence shell model" combines the short range parameters economy of a valence force description with the electronic and mechanical polarizabilities of the shell model. This model has been applied to CdS [4.58], ZnS [4.59] and β -AgI [3.15]. In the latter case, 5 valence force constants and 5 long-range interaction constants (an effective charge, 2 electronic and 2 mechanical polarizabilities) were fitted to the observed phonon dispersion with the results shown in Fig.3.12. The derived density of states is depicted in Fig.3.13.

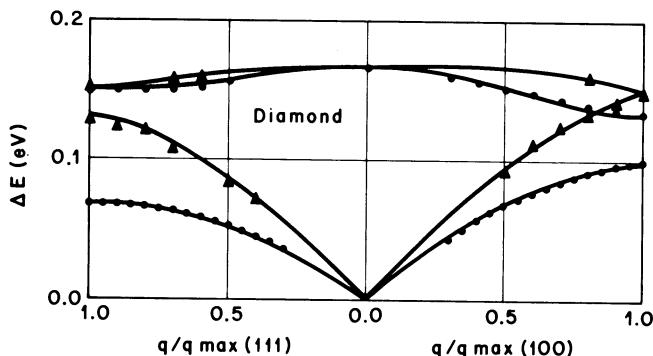


Fig.4.20. Dispersion relations for diamond along (100) and (111) directions. The calculations (solid lines) are based on a valence force model described in the text [4.21]

4.6 Internal and External Vibrations in Molecular Crystals

In this section, we consider crystals containing well-bound molecules or complex ions. Examples are molecular crystals of organic compounds such as hexamethylenetetramine $[(\text{CH}_2)_6\text{N}_4]$, or complex ionic crystals such as CaCO_3 , $(\text{NH}_4)\text{Cl}$, etc. Such crystals generally tend to have complicated structures and a large number of atoms in the primitive unit cell. It is, of course, possible to apply the formalism developed before to such crystals, that is, the dynamics of the atoms could be studied by choosing a suitable model such as the Born-von Karman model or the valence force model. There are, however, serious limitations in practice in applying the formalism to such systems. In the first place, there is the computational difficulty arising from the large number of degrees of freedom per unit cell. Secondly, the physical picture of molecules executing motions as a whole, like translational oscillations and rotational oscillations (librations) is completely lost. It can be reconstructed only after numerical solutions for the displacements of the individual atoms are available.

In order to simplify the problem, one identifies from the beginning the well-bound molecules or complex ions in the crystal and treats them as rigid bodies. These rigid bodies will execute not only translational oscillations but also rotational oscillations. Coupling is allowed for between all the various units in the crystal and the resulting vibrations are called *external vibrations*. The effects of nonrigidity of the molecules or complex ions may be examined separately, thereby treating the effects of the crystal

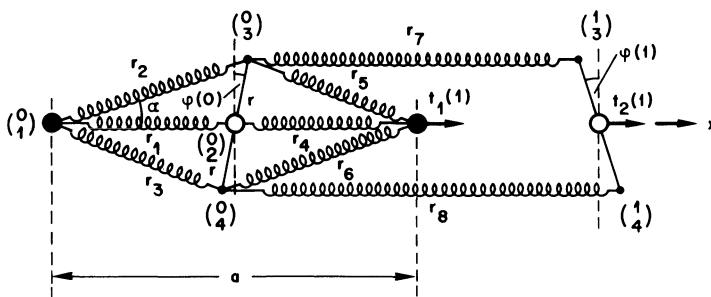


Fig.4.21. A linear chain consisting of alternating atoms (●) and linear rigid XY_2 molecules

upon the molecules considered as a perturbation. This leads to the *internal modes* of the crystal. The frequencies of these internal modes are often very close to the frequencies of the molecules in the gas phase. The basic physical criterion for viewing a group of atoms as well-bound units is that the forces coupling atoms within the group should be much stronger than those coupling the atoms of the group to the remaining crystal. The frequencies of the internal modes will then be considerably higher than those of the external modes. If this is the case, the separation between internal and external modes is a good approximation.

We illustrate the method by considering the linear chain consisting of alternating atoms with mass M_1 and rigid XY_2 molecules with total mass M_2 and moment of inertia Θ (Fig.4.21). The interactions between the different atoms are represented by the 8 stretching coordinates $r_1 \dots r_8$. We consider only motions in the chain direction x. To begin with, we set up the potential energy using the internal coordinate formalism developed in the preceding section. The potential energy per unit cell is

$$2\Phi/N = f(r_1^2 + r_4^2) + g(r_2^2 + r_3^2 + r_5^2 + r_6^2) + h(r_7^2 + r_8^2) . \quad (4.142)$$

It is now an easy exercise to determine the potential energy given by (4.135),

$$2\Phi(q) = \sum_{KK'} M_{KK'}(q) U_K U_{K'}^* , \quad (4.143)$$

where

$$U_K(q) = \frac{1}{\sqrt{N}} \sum_{\lambda} u(\lambda)_K e^{iq\alpha\lambda} \quad (4.144)$$

is the translationally symmetrized Cartesian coordinate of atom K . For the elements of the dynamical matrix $M(q)$, one finds, according to (4.137),

$$\begin{aligned}
 M_{11} &= 2(f + 2c^2g) ; \quad M_{12} = -f(1 + \psi) \\
 M_{13} &= M_{14} = -c^2g(1 + \psi) ; \quad M_{22} = 2f \\
 M_{23} &= M_{24} = 0 ; \quad M_{33} = 2\{c^2g + h[1 - \cos(qa)]\} = M_{44} \\
 M_{34} &= 0 ; \quad M_{k'k'} = M_{kk'} .
 \end{aligned} \tag{4.145}$$

Here, $c = \cos\alpha$ and $\psi = \exp(iqa)$. Now, the motion of a rigid molecule can always be described by specifying the coordinates (t) of its center of gravity and some suitable angles (φ) which specify its orientation. The displacement coordinates of the individual atoms of this molecule are then functions of the coordinates t and φ . From Fig. 4.21 it is apparent that for small displacements t and rotations ω , the following relations hold:

$$\begin{aligned}
 u(\ell_1) &= t_1(\ell) ; \quad u(\ell_3) \approx t_2(\ell) - r\varphi(\ell) , \\
 u(\ell_2) &= t_2(\ell) ; \quad u(\ell_4) \approx t_2(\ell) + r\varphi(\ell) .
 \end{aligned} \tag{4.146}$$

Introducing collective coordinates

$$T_k(q) = \frac{1}{\sqrt{N}} \sum_{\ell} t_k(\ell) e^{iq\alpha\ell} \tag{4.147a}$$

and

$$\phi(q) = \frac{1}{\sqrt{N}} \sum_{\ell} \varphi(\ell) e^{iq\alpha\ell} , \tag{4.147b}$$

we obtain from (4.144, 146)

$$\begin{aligned}
 U_1 &\equiv T_1 ; \quad U_2 \equiv T_2 , \\
 U_3 &= T_2 - r\phi ; \quad U_4 = T_2 + r\phi .
 \end{aligned} \tag{4.148}$$

From (4.148) it is obvious that due to the rigidity of the XY_2 molecules, there are only three independent coordinates. Substituting (4.148) in (4.143) yields

$$\begin{aligned}
 2\Phi &= M_{11} T_1 T_1^* + (M_{22} + 2M_{33}) T_2 T_2^* \\
 &+ (M_{12} + 2M_{13}) T_1 T_2^* + (M_{12}^* + 2M_{13}^*) T_1^* T_2 \\
 &+ 2r^2 M_{33} \dot{\phi} \dot{\phi}^*
 \end{aligned} \tag{4.149}$$

The kinetic energy is given by

$$2T = M_1 \dot{T}_1 \dot{T}_1^* + M_2 \dot{T}_2 \dot{T}_2^* + \theta \dot{\phi} \dot{\phi}^* . \tag{4.150}$$

Using Lagrange equations, one obtains the equations of motion in the usual way and the eigenvalues are

$$\lambda_{1,2} = \frac{f + 2c^2g}{\mu} \left[1 \pm \left(1 - 4 \frac{\mu^2}{M_1 M_2} \sin^2 \left(\frac{aq}{2} \right) \right)^{\frac{1}{2}} \right] , \quad (4.151)$$

where $\mu = M_1 M_2 / (M_1 + M_2)$ and

$$\lambda_3 = \frac{4r^2}{\Theta} \left(c^2 g + 2h \sin^2 \left(\frac{aq}{2} \right) \right) . \quad (4.152)$$

The eigenvalues $\lambda_{1,2}$ are identical to those of the diatomic linear chain (2.36), only f is replaced by the effective force constant $f + 2c^2g$. $\lambda_3(q)$ describes the dispersion of the librational motion of the XY_2 molecules. Due to the symmetry of the problem, there is no coupling between translational and rotational oscillations. The essential features of the dispersion curves are shown in Fig.4.22.

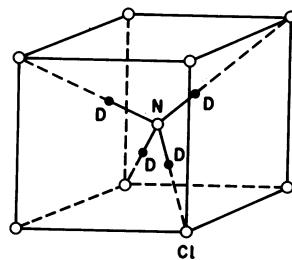
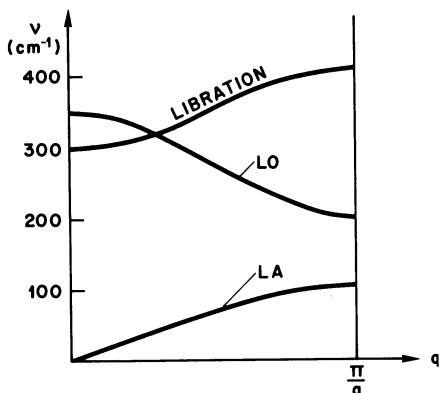


Fig.4.23. Crystal structure of deuterated ammonium chloride, ND_4Cl , at $T < 249.5$ K

Fig.4.22. Dispersion curves for the model illustrated in Fig.4.21. The curves are typical for AgN_3 where N_3 forms a triatomic linear molecule. The force constants used are $f = 0.5$, $g = 0.4$, $h = 0.2$ mdyn/ \AA and $\alpha = 30^\circ$, $r = 1.14$ \AA

An interesting crystal whose external vibrations have been studied along the lines developed here is deuterated ammonium chloride, ND_4Cl , having its ND_4^+ and Cl^- ions in the CsCl structure. Figure 4.23 shows the structure of the ordered state below 249.5 K. The primitive unit cell is a cube and contains one molecule of ND_4Cl , i.e., six atoms, resulting in 18 degrees of freedom. In the external mode approach, one views the unit cell as containing a Cl^- ion and one rigidly bound ND_4^+ ion with a total of nine degrees of freedom, six of which correspond to the translational degrees of freedom

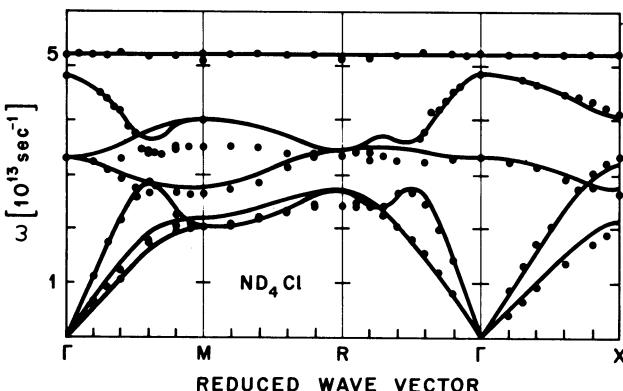


Fig.4.24. Dispersion curves for the external modes of ND_4Cl at 85 K [4.60]. The solid lines are a modified rigid-ion calculation [4.61]

of the Cl^- and ND_4^+ ions and the remaining three to the rotational degrees of freedom of the ND_4^+ ion. The observed phonon dispersion for the external branches is shown in Fig.4.24 [4.60]. The solid line gives the phonon dispersion calculated on the basis of the external mode approach [4.61]. The model adopted contains 7 parameters; it is the rigid-ion model extended to take into account the librational motion of the ND_4^+ ions. The five parameters associated with the translational modes have been determined from the three elastic constants C_{11} , C_{12} , C_{44} and the two long-wavelength optic mode frequencies ω_{T0} and ω_{L0} . The remaining two parameters are associated with the librational motion of the ND_4^+ ions and its coupling to the translational modes. Note that the librational branch near 8.3 THz exhibits a very flat dispersion; this indicates that these excitations can be treated as Einstein oscillators.

4.7 Phonons in Metals

The theory of phonons in metals involves the interaction of the ions with the conduction electrons; strictly speaking, this is outside the scope of this book and therefore only a qualitative discussion will be given. The role of the conduction electrons is to screen out the Coulomb interaction between the positive ions, thereby stabilizing the lattice and reducing considerably the range of interionic forces. It is, therefore, tempting to assume that in a first approximation, the interactions between the screened

ions can be represented by phenomenological short-range forces. We shall discuss below the merits and limitations of this approach.

4.7.1 Force Constant Models

An example of a force constant treatment for Al is shown in Fig.3.18; only three nearest-neighbour force constants have been used whose values have been determined from the three elastic constants. To obtain better agreement, it is necessary to use a large number of force constants extending to at least fifth neighbours [4.62].

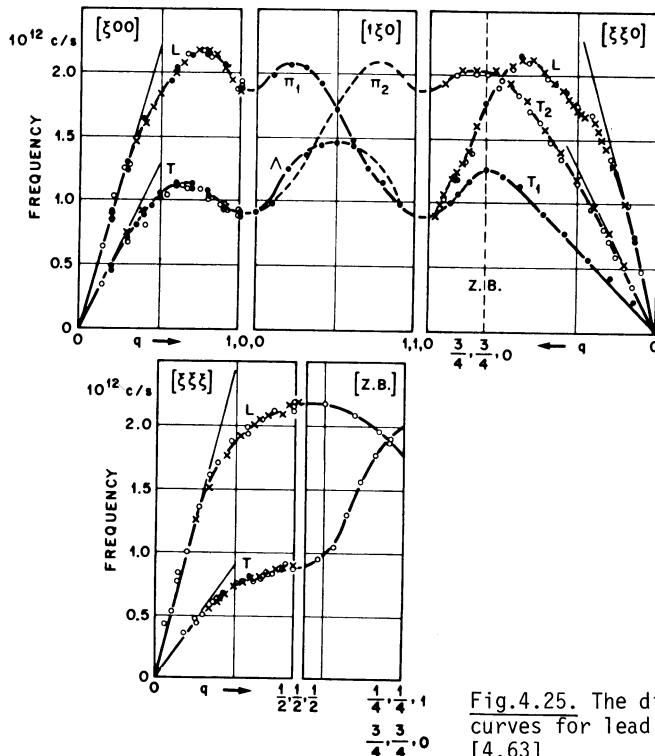


Fig.4.25. The dispersion curves for lead at 100 K [4.63]

The results for lead (Fig.4.25) showed the presence in this metal (and in other polyvalent metals having a large electron-phonon interaction) of interionic forces of long range and complex nature.

The number of independent parameters was found to be too large for a meaningful analysis with the Born-von Karman theory. An analysis in terms of interplanar force constants indicated that measurable forces extend over a distance of more than 20 Å [4.63]. It should be emphasized that this behaviour does not come from some small features in the dispersion curves, but primarily from the large drop in frequency as the zone boundary is approached (Fig.4.25). Besides these general anomalies, the dispersion curves of Fig. 4.25 also show weak, sharp anomalies, for example, in the longitudinal mode for \vec{q} just less than $(1/2, 1/2, 1/2)2\pi/a$; these anomalies require very high Fourier components for an adequate description, and accordingly, suggest the existence of forces of very long range. It was pointed out by KOHN [4.64] that in a metal, an abrupt change in the screening power of the conduction electrons, leading to a logarithmic infinity in the gradient of $\omega_j(\vec{q})$, occurs when $|\vec{\tau} + \vec{q}| = 2k_F$, where $\vec{\tau}$ is a reciprocal lattice vector and k_F is the radius of the Fermi sphere. This is known as the *Kohn anomaly*. In Pb, the observed position of the anomalies are in excellent agreement with accepted dimensions of the Fermi surface.

From the above it is clear that for metals such as Pb and Nb where strong electron-phonon interaction is present, an analysis in terms of phenomenological force constants is not meaningful because the number of force constants is very large and lack physical interpretation.

4.7.2 Coulomb Interaction in the Uniform-Background Lattice Model

In the crudest model, the conduction electrons are represented by a uniform distribution of negative charges which does not respond to the motion of the positive point charges immersed in it. The system is represented in Fig.4.26. The uniform negative charge distribution guarantees the stability and charge neutrality of the system. Each ion is acted on by the sum of the Coulomb forces arising from all the other ions of the lattice plus that resulting from the smeared out charge distribution. The ion-electron interaction just cancels the static ion-ion interaction, so that for the dynamical problem, only the direct Coulomb interactions between the ions must be considered. The phonon dispersion of this system has been studied by CLARK [4.65] using the Ewald method discussed in Sect.4.2.2. The dispersion for phonons propagating along (100) of the bcc lattice is shown in Fig.4.27.

Fairly plausible results were obtained for the TA-modes, but the LA-mode has the characteristics of an optic branch in that it approaches a non-vanishing frequency $\omega_{LA}(0)$ for $q \rightarrow 0$ given by

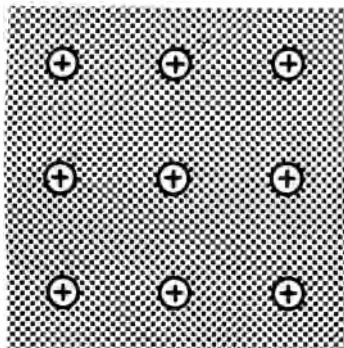


Fig.4.26. Uniform-background lattice model: the positive point ions are immersed in a uniform negative background formed by the conduction electrons which do not respond to the motion of the ions

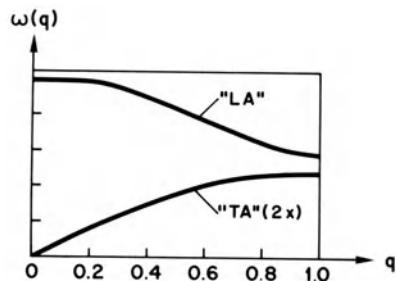


Fig.4.27. Dispersion of the TA and "LA" phonons in the (100) direction of the bcc lattice according to the uniform-background model [4.65]

$$\omega_{\text{LA}}^2(0) = \frac{4\pi(Ze)^2}{mv_a} , \quad (4.153)$$

where v_a is the volume of the unit cell. This is the ionic plasma frequency which can be derived in a similar way to the well-known electronic plasma frequency [4.66]. However, from experiments we know that $\omega_{\text{LA}}(q)$ vanishes linearly with q . The nonphysical result (4.153) is not obtained when the conduction electrons are allowed to adjust to the motion of the ions and screen out the Coulomb interaction of the latter.

4.7.3 Bardeen's Treatment of Screening

For an alkali metal, an approximate theory of the lattice dynamics can be developed as follows [4.67]. We first consider an ion with a positive charge distribution $Z(r)$ for which $\int Z(r)d^3r = Z$ and let $Z(Q)$ be its Fourier transform defined by

$$Z(Q) = \int d^3r Z(r) e^{i\vec{Q}\cdot\vec{r}} ,$$

and conversely,

$$Z(r) = \frac{1}{(2\pi)^3} \int d^3Q Z(Q) e^{-i\vec{Q}\cdot\vec{r}} ,$$

from which it follows that

$$Z(Q = 0) = Z . \quad (4.154)$$

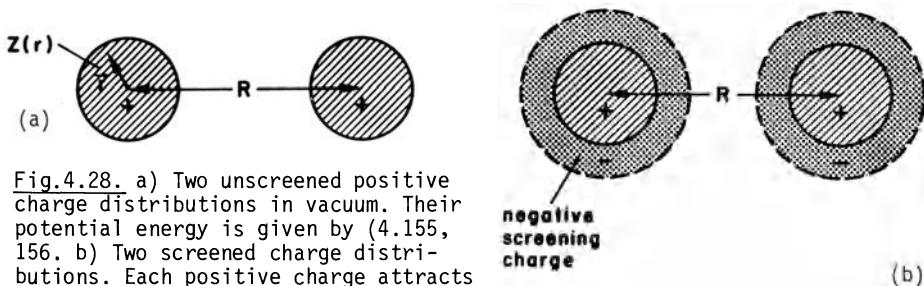


Fig.4.28. a) Two unscreened positive charge distributions in vacuum. Their potential energy is given by (4.155, 156). b) Two screened charge distributions. Each positive charge attracts a negative charge cloud. The potential energy is given by (4.157-159)

Now we consider two such charge distributions separated by a distance R in vacuum (Fig.4.28a). The potential energy of the two unscreened charges is

$$\varphi(R)_{\text{unscr}} = \frac{1}{(2\pi)^3} \int d^3Q \varphi(Q)_{\text{unscr}} e^{-i\vec{Q}\vec{R}} . \quad (4.155)$$

By arguments similar to those outlined in Appendix K [(K.17,18)], it follows that

$$\varphi(Q)_{\text{unscr}} = \frac{4\pi Z^2(Q)}{Q^2} . \quad (4.156)$$

We now suppose that the two charge distributions are immersed in a free electron gas. The positive ions will attract a screening charge (Fig.4.28b). It is as if the conduction electrons formed a charge cloud amounting to Z -electrons around each ion. This screening charge is to be regarded as moving with each ion. The potential energy of the two screened charges is now

$$\varphi(R)_{\text{scr}} = \frac{1}{(2\pi)^3} \int d^3Q \varphi(Q)_{\text{scr}} e^{-i\vec{Q}\vec{R}} . \quad (4.157)$$

It was first shown by BARDEEN [4.68] that in the Hartree approximation (that is, neglecting both exchange and correlation),

$$\varphi(Q)_{\text{scr}} = \frac{\varphi(Q)_{\text{unscr}}}{\epsilon(Q)} = \frac{4\pi Z^2(Q)}{Q^2 \epsilon(Q)} , \quad (4.158)$$

where the dielectric function $\epsilon(Q)$ is given by

$$\epsilon(Q) = 1 + \frac{6\pi n e^2}{Q^2 E_F} \left[\frac{1}{2} + \frac{4k_F^2 - Q^2}{8k_F Q} \ln \frac{|2k_F + Q|}{|2k_F - Q|} \right] . \quad (4.159)$$

In this equation, n is the conduction electron density, E_F the Fermi energy and k_F the radius of the Fermi sphere. $\epsilon(Q)$ given by (4.159) is also known as the *Lindhard dielectric constant* [4.69]. For $Q \rightarrow 0$, the quantity in the square brackets is equal to 1 and $\epsilon(Q)$ then reduces to the *Thomas-Fermi dielectric function* [4.69].

We now imagine the positive charge distributions to be arranged on a lattice and assume that this is not inconsistent with the electrons remaining free. This system represents a rough model of a metallic crystal; for consistency, we must assume that the electron density is $n = Z/v_a e$ where v_a is the cell volume. For one atom per unit cell, the equations of motion are

$$m\omega^2(\vec{q})u_\alpha(\vec{q}) = \sum_\beta M_{\alpha\beta}(\vec{q})u_\beta(\vec{q}) , \quad (4.160)$$

where

$$M_{\alpha\beta}(\vec{q}) = N_{\alpha\beta}(\vec{q}) - N_{\alpha\beta}(0) \quad (4.161)$$

and

$$N_{\alpha\beta}(\vec{q}) = - \sum_{\ell'} \left(e^{i\vec{q}\vec{R}} \frac{\partial^2 \varphi(R)}{\partial R_\alpha \partial R_\beta} \right) \vec{r} = \vec{r}(\ell') - \vec{r}(\ell) , \quad (4.162)$$

with $\varphi(R)_{scr}$ given by (4.157). Following a derivation paralleling the one given in Appendix K, we obtain for a Bravais lattice

$$N_{\alpha\beta}(\vec{q}) = \frac{1}{v_a} \sum_{\vec{\tau}} (\vec{\tau} + \vec{q})_\alpha (\vec{\tau} + \vec{q})_\beta \varphi(\vec{\tau} + \vec{q})_{scr} , \quad (4.163)$$

where $\varphi(\vec{\tau} + \vec{q})_{scr}$ is given by (4.158). The analogous expression for a lattice with a basis is given by (K.16).

We now demonstrate that in contrast to the uniform-background model (Fig.4.26), the frequency $\omega_{LA}(\vec{q})$ vanishes linearly with \vec{q} . For this purpose, we consider a longitudinal mode with \vec{q} parallel to the x -direction of the cubic monoatomic crystal. By symmetry, $u_y(\vec{q}) = u_z(\vec{q}) = 0$ for this case and (4.160) reduces to

$$m\omega^2(\vec{q}) = M_{xx}(\vec{q}) . \quad (4.164)$$

Now consider sound waves for which $q \rightarrow 0$, and for simplicity we assume that $Z(Q)$ falls off sufficiently rapidly that the only reciprocal lattice point which contributes to the sum in (4.163) is $\vec{\tau} = 0$. We then obtain

$$m\omega^2 = \frac{1}{v_a} \left[q^2 \phi(q)_{scr} - \lim_{q \rightarrow 0} q^2 \phi(q)_{scr} \right] . \quad (4.165)$$

From (4.159), it follows that

$$\epsilon(q \rightarrow 0) \approx \frac{6\pi Ze}{v_a q^2 E_F}$$

and

$$\varphi(q \rightarrow 0)_{scr} \approx \frac{2Z^2(0)v_a E_F}{3Ze} .$$

Thus we obtain

$$m\omega^2(q \rightarrow 0) \approx \frac{2}{3} q^2 \frac{Z}{3} E_F$$

and the velocity of sound is given by

$$v^2 = \frac{\omega^2}{q^2} = \frac{2}{3} \frac{E_F}{m_e} \frac{Z}{e} . \quad (4.166a)$$

This is the *Bohm-Staver relation* [4.70]. Since $E_F = m_e v_F^2 / 2$, where m_e is the electron mass and v_F the Fermi velocity, we can write

$$v^2 = \frac{1}{3} \frac{Z}{e} \frac{m_e}{m} v_F^2 . \quad (4.166b)$$

Since the electron to ion mass ratio is typically of the order of 10^{-4} or 10^{-5} , this predicts a sound velocity about a hundredth of the Fermi velocity or of the order of 10^4 m/s in agreement with observed orders of magnitude.

The Kohn anomaly mentioned in Sect.4.7.1 is due to the fact that the Lindhard dielectric constant $\epsilon(q)$ given by (4.159) becomes singular when the wave vector \vec{q} of the phonon has magnitude $2k_F$. In three-dimensional metals, this results in the weak "kinks" in $\omega(\vec{q})$ at $q = 2k_F$ (Fig.4.25). In one-dimensional metals, the electron-phonon interaction produces much stronger Kohn anomalies than in three-dimensional metals. In fact, a giant Kohn anomaly has been observed in the one-dimensional conductor KCP [1.35]. For a more detailed discussion of the theory of phonons in metals, the reader is referred to [4.66] and to the work by HARRISON [4.71] in which the *pseudopotential approximation* is used. This latter method yields good agreement between calculated and observed phonon frequencies of simple metals such as aluminium with only two model parameters.

4.8 Problems

4.8.1 Lennard-Jones Parameters of the Linear Chain with Zero-Point Energy

Consider a monoatomic linear chain of atoms with mass m and nearest-neighbour interactions of the Lennard-Jones type with $\varphi(r)$ given by (4.2). Prove that the zero-point energy

$$E_0 = \frac{1}{2} \sum_q m\omega(q)$$

is given by

$$E_0 = \frac{2Nk}{\pi\sqrt{m}} \sqrt{\varphi''(r)} ,$$

where $\varphi''(r) = d\varphi/dr^2$.

From (4.5,7,8) with $P = 0$ and the result obtained above, show that

$$\varphi(r_0) + \frac{2k}{\pi\sqrt{m}} \sqrt{\varphi''(r_0)} = -L_0 ,$$

$$\varphi'(r_0) + \frac{k}{\pi\sqrt{m}} \frac{\varphi'''(r_0)}{\sqrt{\varphi''(r_0)}} = 0 ,$$

where r_0 and $L_0 = -F/N$ are the equilibrium lattice constant and the heat of sublimation, respectively. If r_0 and L_0 are known from experiments, the above two equations allow the determination of the Lennard-Jones parameters σ and ϵ . Similar relations can be derived for three-dimensional crystals [4.72].

4.8.2 Shell Model of the Linear Monoatomic Chain

Consider a linear chain of identical atoms as illustrated in Fig.4.29.

Let $u(\ell)$ and $v(\ell)$ be the displacements of the core and shell, respectively, of atom ℓ . Show that the dispersion relation of the longitudinal modes is given by

$$m\omega^2(q) = \frac{4S \sin^2(\frac{qa}{2})}{1 + 4 \frac{S}{k} \sin^2(\frac{qa}{2})} .$$

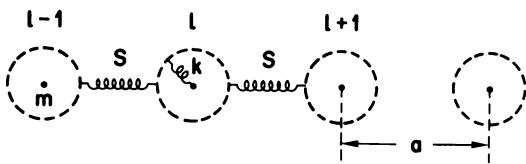


Fig.4.29. Shell model of the monoatomic linear chain. The core mass is m

4.8.3 Generalized Lyddane-Sachs-Teller Relation

Consider a dielectric constant of the form

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{S_1}{\omega_{T1}^2 - \omega^2} + \frac{S_2}{\omega_{T2}^2 - \omega^2}$$

which is a special case of (4.115). Show directly from the above equation that

$$\frac{\epsilon_0}{\epsilon_{\infty}} = \frac{\omega_{L1}^2 \omega_{L2}^2}{\omega_{T1}^2 \omega_{T2}^2}$$

and that

$$S_j = \epsilon_{\infty} (\omega_{Lj}^2 - \omega_{Tj}^2) .$$

Hint: Note that $\epsilon(\omega_{Lj}) = 0$. Write the condition $\epsilon = 0$ as a second degree polynomial in $x = \omega^2$ and note that the roots x_1 and x_2 of the quadratic equation $x^2 + bx + c = 0$ are given by $x_1 x_2 = c$ and $x_1 + x_2 = -b$. The proof can be easily extended to a dielectric constant of the form (4.115) representing n undamped oscillators.

4.8.4 Bending Coordinates: Application to the Linear Chain

Consider the monoatomic linear chain illustrated in Fig.4.30. The potential energy per unit cell is $\phi/N = f(a\Delta\alpha_0)^2/2$, where f is the bending force constant and $a\Delta\alpha_0 = u_{-1} + u_1 - 2u_0$. Using the results of Sect.4.5, show that the dispersion relation for transverse vibrations is given by

$$\omega(q) = 4\sqrt{\frac{f}{m}} \sin^2\left(\frac{qa}{2}\right).$$

For $q \ll \pi/a$, one obtains $\omega(q) \sim q^2$! This starting result indicates that such a system is "dispersive" even at infinite wavelength!

In three-dimensional crystals, this result is important for layer compounds such as graphite: the transverse out-of-plane vibrations with \vec{q} parallel to the layers can be adequately described by bending coordinates

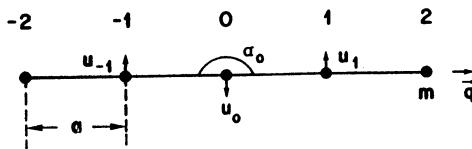


Fig. 4.30. Transverse modes of the linear chain described by bending coordinates α

and for a single layer, one obtains $\omega(q) = Bq^2$ for $q \rightarrow 0$. However, the very weak interplane coupling gives rise to a term Aq so that $\omega(q) = Aq + Bq^2$ for small q ; such a dispersion relation has been observed in graphite. At sufficiently low frequencies, $Aq \gg Bq^2$ and the elastic continuum analysis is appropriate. For a detailed discussion of this result and its implications to the specific heat, see [4.73-76].

4.8.5 Thomas-Fermi Screening

According to (4.157), the potential energy of two charges separated by a distance R is

$$\varphi(R) = \frac{1}{(2\pi)^3} \int d^3q \varphi(q) e^{-iq\vec{R}} .$$

For two-point charges of magnitude Z , the Thomas-Fermi screening theory gives the result [4.69]

$$\varphi(q) = \frac{4\pi Z^2}{k_0^2 + q^2} ,$$

where k_0 is the Thomas-Fermi wave vector. Show that if this expression is substituted in the above integral, the result is

$$\varphi(R) = \frac{Z^2}{R} e^{-k_0 R} .$$

$\varphi(R)/R$ is known as the *screened Coulomb potential* or *Yukawa potential*. Thus, the potential energy is of the Coulombic form times an exponential damping factor that reduces it to a negligible size at distances greater than order $1/k_0$. For a free electron gas, k_0 is of the order of k_F .

Hint: Evaluate the integral in spherical coordinates and use the result

$$\int_0^\infty \frac{x \sin(ax)}{b^2 + x^2} dx = \frac{\pi}{2} e^{-ab} .$$

5. Anharmonicity

The theory of lattice vibrations which we discussed in the preceding chapters has been based on the harmonic approximation which neglects all terms in the expansion of the potential energy (3.6) higher than the second-order terms. The most important consequences of the harmonic approximations are:

- a) there is no thermal expansion;
- b) the force constants and hence the elastic constants are independent of temperature and pressure;
- c) the heat capacity becomes constant at high temperatures;
- d) the specific heats measured at constant pressure and constant volume are equal: $c_p = c_v$;
- e) since there are no collisions between phonons, their mean free paths and lifetimes are infinite;
- f) as a consequence of (e), a perfectly harmonic crystal would have an infinite thermal conductivity;
- g) the line widths of the infrared absorption peaks and of the Raman, Brillouin and inelastic neutron scattering peaks are zero for perfectly-ordered harmonic crystals.

In real crystals, none of these consequences is satisfied accurately.

As an introduction, the chapter begins with the anharmonic diatomic molecule. Then we study the thermal properties (free energy, equation of state, thermal expansion and specific heat) of the classical anharmonic linear chain. Two important concepts are introduced: the *Grüneisen parameter* and the *quasiharmonic approximation*¹. In this approximation, the temperature dependence of the force constants and phonon frequencies is *only* due to the

¹ In the literature, different definitions of the quasiharmonic approximation are used. Here, we adopt the definition of LEIBFRIED and LUDWIG [5.54]

effects of thermal expansion. The study of the anharmonic chain includes the calculation of the specific heat which is shown to increase linearly with T at high temperatures. To obtain this result, it is necessary to go beyond the quasiharmonic approximation and include the specific anharmonic term in the free energy. In Sect.5.3, we study the *equation of state* of three-dimensional crystals on the basis of the quasiharmonic approximation in the quantum mechanical treatment. We also give a discussion of anharmonic effects on the specific heat and elastic constants.

The *self-consistent harmonic approximation* (SCHA) developed in Sect.5.4 is a method for crystals with strong anharmonicity such as the rare-gas solids. The SCHA has also been applied to the study of soft modes in ferroelectric phase transitions and to the melting process.

In the last section, we introduce the *response function* for an anharmonic crystal. The response function depends on *frequency widths and shifts* which are evaluated on the basis of perturbation theory. This is the *pseudoharmonic approximation* which includes not only the effects of thermal expansion (as in the quasiharmonic approximation), but also the effects of phonon-phonon interactions. Both the widths (damping) and shifts depend on temperature and on the frequency with which the crystal is "probed".

5.1 The Anharmonic Diatomic Molecule

The potential energy of a diatomic molecule is illustrated in Fig.5.1. A mathematical expression that actually represents a potential curve of this form and which is often used for molecules has been proposed by MORSE [5.1]. It is

$$\varphi(r) = D[1 - e^{-\lambda(r-a_0)}]^2 \quad . \quad (5.1)$$

Here, D is the dissociation energy and λ is a positive constant.

For very small amplitudes of vibration ($T = 0$), the mean separation between the atoms is a_0 for the classical case. For large amplitudes (high temperatures), however, the mean separation will be $a > a_0$ due to the deviations of $\varphi(r)$ from the parabolic curve. This is the qualitative explanation of thermal expansion. Let

$$w_0 = r - a_0 \quad (5.2)$$

be the change in distance with respect to a_0 . Expanding $\varphi(r)$ in a power series, we obtain

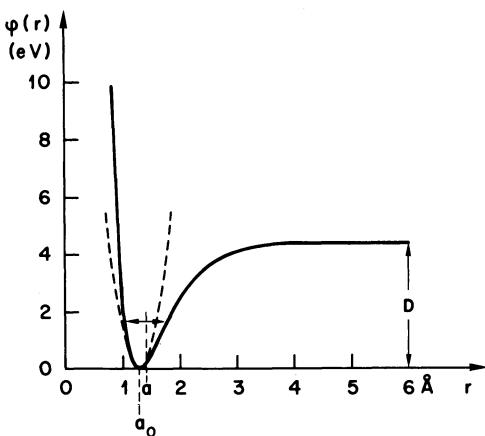


Fig.5.1. Potential energy of a diatomic molecule after MORSE, as defined by (5.1). The parameters are those of the electronic ground state of the HCl molecule: $D=4.43 \text{ eV}$, $\lambda=1.9047 \cdot 10^8 \text{ cm}^{-1}$, $a_0=1.2745 \text{ \AA}$. a is the mean interatomic distance at temperature T . The dashed curve indicates the corresponding harmonic potential energy

$$\phi(r) = \frac{1}{2} f_0 w_0^2 + \frac{1}{3!} g_0 w_0^3 + \frac{1}{4!} h_0 w_0^4 + \dots , \quad (5.3)$$

where the subscript 0 indicates that we have expanded around a_0 . For the Morse potential, we obtain for the force constants the expressions

$$f_0 = 2\lambda^2 D > 0, \quad g_0 = -6\lambda^3 D < 0, \quad h_0 = 14\lambda^4 D > 0 .$$

We note that g_0 is, in general, a *negative constant*. Neglecting the quartic anharmonic term in (5.3), the equation of motion can be written in the form

$$\ddot{w}_0 + \omega_0^2 w_0 + s w_0^2 = 0 , \quad (5.4)$$

where

$$\omega_0^2 = f_0/\mu \quad (5.5)$$

(μ = reduced mass) and

$$s = g_0/2f_0 . \quad (5.6)$$

Now we look for a solution of the form

$$w_0 = v_0 + A(\cos \omega t + \eta \cos 2\omega t) . \quad (5.7)$$

In (5.7) we have included the first three terms of the Fourier expansion of the motion. If we retained the term proportional to w_0^3 in (5.4), the expansion (5.7) would also contain a term proportional to $\cos 3\omega t$. Physically it is clear that the Fourier decomposition of the motion of a sphere in a potential as illustrated in Fig.5.1 contains not only the frequency ω (harmonic term), but also the overtones 2ω , 3ω , etc. Substituting (5.7) in (5.4), assuming $sA \ll 1$ and neglecting in w_0^2 terms in η and v_0 , one obtains

$$v_0 = -\frac{1}{2} sA^2 > 0 , \quad (5.8)$$

$$\omega^2 = \omega_0^2(1 - s^2 A^2) , \quad (5.9)$$

$$\eta = sA/6 . \quad (5.10)$$

The time average of the interatomic separation is given by

$$\begin{aligned} \langle r \rangle &= a = a_0 + \langle w_0 \rangle = a_0 + v_0 , \\ &= a_0 - \frac{1}{2} sA^2 = a_0 - \frac{1}{4} \frac{g_0}{f_0} A^2 . \end{aligned} \quad (5.11)$$

Here we have used (5.7) and the fact that $\langle \cos \omega t \rangle = \langle \cos 2\omega t \rangle = 0$. Equation (5.11) means that the mean distance a is larger than a_0 . The force constant f (curvature of $\phi(r)$ at $r = a$) is smaller than the force constant f_0 (curvature of $\phi(r)$ at $r = a_0$); this gives rise to a decrease of the frequency as expressed by (5.9).

Suppose that the molecule is in thermal equilibrium with a heat bath at temperature T . Its mean vibrational energy is then given by $\bar{E} = \mu \omega^2 A^2 / 2 \approx \mu \omega_0^2 A^2 / 2 = f_0 A^2 / 2 = k_B T$ at high temperatures. Hence

$$A^2 = \frac{2k_B T}{f_0} \quad (5.12)$$

and from (5.11), we obtain

$$a(T) \approx a_0 - \frac{1}{2} \frac{g_0}{f_0^2} k_B T . \quad (5.13)$$

We note that $a(T) > a_0$ since $g_0 < 0$. The relation (5.13) represents the thermal expansion of the diatomic molecule. Substituting (5.6,12) in (5.9), we obtain for the renormalized frequency

$$\omega^2(T) = \omega_0^2 \left(1 - \frac{g_0^2}{2f_0^3} k_B T \right) . \quad (5.14)$$

It is possible to obtain the results (5.13,14) by directly evaluating the thermodynamical averages of a and the force constant f (Problem 5.6.1). By starting with the equation of motion (5.4) and its solution (5.7), we have, in addition, gained some insight into the dynamics of the system. The dynamics of a polyatomic anharmonic molecule with several fundamental frequencies ... ω_k ... ω_ℓ ... is more complicated. Its vibrational motion will not only contain the frequencies ω_k , $2\omega_k$, $3\omega_k$... as in the diatomic molecule, but in

addition, the combinations $\omega_k \pm \omega_\ell$, $2\omega_k \pm \omega_\ell$, etc. Therefore, in the infrared and Raman spectra, in addition to the fundamentals, overtones and combination vibrations may also occur [5.2].

5.2 The Anharmonic Linear Chain

5.2.1 Dynamical Aspects

The equations of motion for an anharmonic linear and monoatomic chain with nearest-neighbour interactions are

$$\begin{aligned} m\ddot{u}_\ell &= f[u_{\ell+1} - u_\ell] - (u_\ell - u_{\ell-1})] \\ &\quad + \frac{1}{2} g[(u_{\ell+1} - u_\ell)^2 - (u_\ell - u_{\ell-1})^2] \\ &\quad + \frac{1}{6} h[(u_{\ell+1} - u_\ell)^3 - (u_\ell - u_{\ell-1})^3] + \dots . \end{aligned} \quad (5.15)$$

A solution of these equations is very complicated, especially for strong anharmonicity. For the harmonic chain ($g = h = 0$), the solution can be written in the form of plane waves. On the other hand, for a diatomic anharmonic molecule it is possible to write down a solution of the form (5.7). Such simple solutions do not exist for (5.15); the difficulty arises from the propagation of the excitations in a nonlinear system.

For the case of weak anharmonicity, the basic principle of solution is the following: one uses the solution of the harmonic lattice as a basis set and treats the nonlinearity in perturbation theory. This leads to a shift in the energy of the phonons and to a finite lifetime of them. We shall discuss this theory in Sect. 5.5 and confine ourselves to a short review of its development here.

A perturbation treatment of anharmonic systems was first performed by DEBYE in 1914 [5.3]. In 1925, PAULI calculated the damping constant Γ for infrared absorption by a monoatomic linear chain of the form (5.15) but composed of atoms with alternating positive and negative charges. He obtained the result [5.4]

$$\Gamma = \frac{4\epsilon^2 k_B T}{m\omega_0^2} , \quad (5.16)$$

where $\epsilon = g/2m\omega_0^2$ and $\omega_0^2 = f/m$. In 1929, PEIERLS developed his famous theory of heat conduction [5.5]. Based on PEIERLS' perturbation treatment, BORN

and BLACKMAN [5.6] extended PAULI's calculation. It turned out that for unequal masses, Γ is not a constant anymore but depends on the frequency of the infrared light. The maxima of $\Gamma(\omega)$ appear at positions $\omega = \omega_1 \pm \omega_2$, where ω_1 and ω_2 are the optic and acoustic zone boundary frequencies. This mechanism leads to the multiphonon absorption to be discussed in [1.35].

More recently, Green's function methods have been applied to evaluate analytic expressions of phonon frequencies and widths as well as of thermodynamic properties of the linear chain [5.7-9]. These studies have shown that the complex anharmonic self-energies, that is, the shifts and widths of the phonon energies, depend on q and on the applied frequency ω . The results of such calculations for three-dimensional crystals will be discussed in Sect.5.5.

Finally we mention the interesting new developments in this field. KRUMHANSL and SCHRIEFFER have studied the dynamics and statistical mechanics of a one-dimensional model system whose displacement field Hamiltonian is strongly anharmonic [5.10]. The most important result is that the phonon representation commonly used in perturbation calculations is inadequate for discussing one important type of excitation which can occur in highly non-linear systems. This excitation corresponds to domain-wall motion and is now called a *soliton* [5.11,12]. A qualitative discussion of solitons will be given in [1.35].

5.2.2 The Free Energy of the Classical Anharmonic Chain

The one-dimensional model considered here is the only system for which the free energy F can be evaluated without crude approximations. In the three-dimensional case, F is a function of the temperature T and the volume V and the *equation of state* is given by (Sect.5.3.1)

$$P = - \left(\frac{\partial F}{\partial V} \right)_T . \quad (5.17)$$

The internal energy U and the entropy S are given by the relations

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V = F + TS \quad (5.18)$$

and the specific heat is defined by

$$c_V = \left(\frac{\partial U}{\partial T} \right)_V . \quad (5.19a)$$

The relation between c_P and c_V is

$$c_p = c_V + T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P . \quad (5.19b)$$

The analogous relations for the chain are obtained by replacing V by the length L of the chain and the pressure P by the force K acting on the chain.

The free energy is defined by

$$F = -k_B T \ln(Z) = -\beta^{-1} \ln(Z) . \quad (5.20)$$

For a classical system whose kinetic energy T depends only on the momenta p and whose potential energy ϕ is a function of the coordinates q only, the partition function Z is given by

$$Z = A \cdot Z_T \cdot Z_\phi , \quad (5.21)$$

where

$$Z_T = \int e^{-\beta T(p)} dp \quad (5.22)$$

and

$$Z_\phi = \int e^{-\beta \phi(q)} dq . \quad (5.23)$$

The constant A is given by $A = (N!h^{sN})^{-1}$, where N is the number of particles, h is Planck's constant and s is the degree of freedom of each particle. The thermodynamic quantities of interest such as U , c_V , c_p , etc., are independent of A .

We consider a chain of $N + 1$ identical atoms with mass m and nearest-neighbour interactions [5.13]. For $T = 0$ and external force $K = 0$, the lattice spacing is a_0 and the change in distance between atoms ℓ and $\ell - 1$ due to atomic displacements $u_{0,\ell}$ and $u_{0,\ell-1}$ is $w_{0,\ell} = u_{0,\ell} - u_{0,\ell-1}$ (Fig.5.2a). Just as for the diatomic molecule considered in Sect.5.1, the interatomic distance will change due to thermal expansion. Let $a(T,K)$ be the lattice spacing at temperature T and external force K . The change in distance between atoms ℓ and $\ell - 1$ due to their atomic displacements u_ℓ and $u_{\ell-1}$ is now $w_\ell = u_\ell - u_{\ell-1}$ (Fig.5.2b).

The deformation $\epsilon(T,K)$ is defined by

$$a(T,K) = [1 + \epsilon(T,K)]a_0 . \quad (5.24)$$

a_0 is defined by the minimum of the potential energy ϕ while $a(T,K)$ is obtained from (5.17). For nearest-neighbour interactions, ϕ can be written in the form

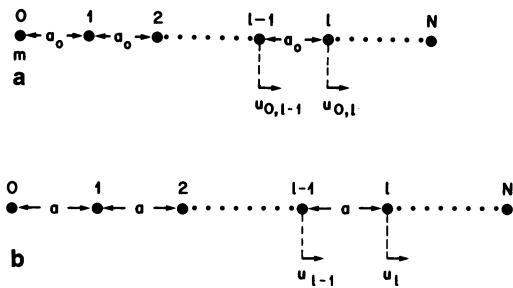


Fig.5.2. a) Linear monoatomic chain at $T = 0$ and $K = 0$ with lattice spacing a_0 . b) Chain at temperature T under the influence of an external force K with lattice spacing $a = a(T, K)$

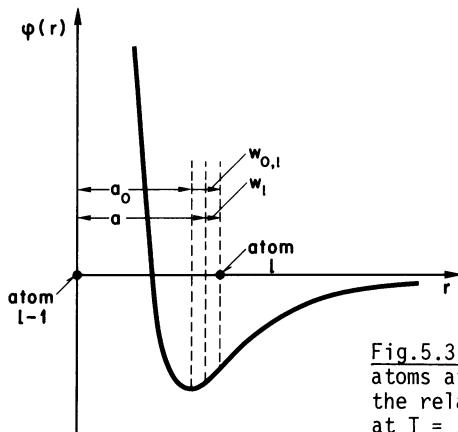


Fig.5.3. Interaction energy of two neighbouring atoms at positions r_ℓ and $r_{\ell-1}$. $w_{0,\ell}$ and w_ℓ are the relative displacements with respect to a_0 at $T = K = 0$ and $a(T, K)$, respectively

$$\Phi = \sum_{\ell=1}^N \varphi(r_\ell - r_{\ell-1}) \quad , \quad (5.25)$$

where $\varphi(r_\ell - r_{\ell-1})$ is the interaction energy between atoms at positions r_ℓ and $r_{\ell-1}$. The shape of $\varphi(r)$ is similar to that of the diatomic molecule (Fig.5.1) and is shown in Fig.5.3. From Fig.5.3 it is evident that

$$\varphi(r_\ell - r_{\ell-1}) = \varphi(a_0 + w_{0,\ell}) = \varphi(a + w_\ell) \quad . \quad (5.26)$$

Expansion of φ up to the fourth order gives

$$\varphi(a_0 + w_0) = \varphi(a_0) + \frac{1}{2} f_0 w_0^2 + \frac{1}{3!} g_0 w_0^3 + \frac{1}{4!} h_0 w_0^4 \quad (5.27)$$

and

$$\varphi(a + w) = \varphi(a) + ew + \frac{1}{2} fw^2 + \frac{1}{3!} gw^3 + \frac{1}{4!} hw^4 \quad . \quad (5.28)$$

Note that in (5.28), $e = (\partial\varphi/\partial w)_a \neq 0$. For later reference, we establish relations between the force constants appearing in (5.27,28). Substituting

$w_0 = a_0 \varepsilon + w$ in (5.27) and comparing with (5.28) gives

$$\varphi(a) = \varphi(a_0) + \frac{1}{2} f_0(a_0 \varepsilon)^2 + \frac{1}{3!} g_0(a_0 \varepsilon)^3 + \frac{1}{4!} h_0(a_0 \varepsilon)^4 , \quad (5.29a)$$

$$e(\varepsilon) = f_0 a_0 \varepsilon + \frac{1}{2} g_0(a_0 \varepsilon)^2 + \frac{1}{3!} h_0(a_0 \varepsilon)^3 , \quad (5.29b)$$

$$f(\varepsilon) = f_0 + g_0 a_0 \varepsilon + \frac{1}{2} h_0(a_0 \varepsilon)^2 , \quad (5.29c)$$

$$g(\varepsilon) = g_0 + h_0 a_0 \varepsilon , \quad (5.29d)$$

$$h(\varepsilon) = h_0 . \quad (5.29e)$$

The free energy has to be evaluated with the constraint that $L = Na$ is the length of the chain. Since $L = r_N - r_0$, we have $r_N - r_0 - Na = 0$
 $= (r_N - r_{N-1} - a) + \dots (r_\ell - r_{\ell-1} - a) + \dots + (r_1 - r_0 - a) = w_N + \dots + w_\ell + \dots w_1$; hence the constraint can be written in the form

$$\sum_{\ell=1}^N w_\ell = 0 . \quad (5.30)$$

From (5.25, 26, 28, 30), it follows that

$$\Phi = N\varphi(a) + \sum_{\ell=1}^N \psi(w_\ell) , \quad (5.31)$$

where

$$\psi(w_\ell) = \frac{1}{2} f w_\ell^2 + \frac{1}{3!} g w_\ell^3 + \frac{1}{4!} h w_\ell^4 . \quad (5.32)$$

Concerning the kinetic energy, we assume the center-of-mass velocity to vanish; this gives a relation between the momenta of the $N + 1$ atoms so that only N independent momenta p_ℓ are left which make the usual contribution $p_\ell^2/2m$ to the kinetic energy. (This can be seen most easily if the center of mass coincides with a lattice particle, as is the case for an uneven number of atoms). The kinetic energy is therefore given by

$$T = \sum_{\ell=1}^N \frac{p_\ell^2}{2m} . \quad (5.33)$$

Substitution of (5.33) in (5.22) gives

$$Z_T = \left[\int_{-\infty}^{+\infty} \exp\{-\beta/2m\} p^2 dp \right]^N = (2\pi m k_B T)^{N/2} . \quad (5.34)$$

From (5.23,31) it follows that

$$Z_\Phi = e^{-\beta N \varphi(a)} \int_{-\infty}^{+\infty} e^{-\beta \sum \psi(w_\ell)} dw_1 \dots dw_N \quad (5.35)$$

which has to be evaluated with the constraint (5.30). Introducing the constraint in the form of a δ -function in the integrand of (5.35), we obtain

$$Z_\Phi = e^{-\beta N \varphi(a)} \int_{-\infty}^{+\infty} e^{-\beta \sum \psi(w_\ell)} \delta(\sum w_\ell) dw_1 \dots dw_N .$$

Using the integral representation of the δ -function

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-isx} ds , \quad (5.36)$$

it follows that

$$\begin{aligned} Z_\Phi &= \frac{1}{2\pi} e^{-\beta N \varphi(a)} \int_{-\infty}^{+\infty} ds \int_{-\infty}^{+\infty} \exp \left\{ - \sum_{\ell=1}^N [\beta \psi(w_\ell) + i s w_\ell] \right\} dw_1 \dots dw_N \\ &= \frac{1}{2\pi} e^{-\beta N \varphi(a)} \int_{-\infty}^{+\infty} e^{Nz(s)} ds , \end{aligned} \quad (5.37)$$

where

$$\begin{aligned} e^{z(s)} &= \int_{-\infty}^{+\infty} e^{-\beta \psi(w) - i s w} dw \\ &\approx \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\beta f w^2} (1 - v + \frac{1}{2} v^2 - \frac{1}{3!} v^3) dw , \end{aligned} \quad (5.38)$$

with

$$v = \beta(Gw^3 + Hw^4) + iws$$

and $G = g/3!$, $H = h/4!$. The integrations in (5.38) can easily be carried out. Since N is large, the integral in (5.37) can be evaluated by the saddle-point method [5.14] (Appendix M).

The final result for the free energy given by (5.20) is

$$F(T, \epsilon) = \Phi_{e1} + F_{vib} + F_{anh} - k_B T \ln A , \quad (5.39)$$

where

$$\Phi_{e1} = N \varphi(a) , \quad (5.40)$$

$$F_{vib} = -\frac{N}{2} k_B T \left[\ln(2\pi m k_B T) + \ln \frac{2\pi k_B T}{f} \right] , \quad (5.41)$$

$$F_{\text{anh}} = N(k_B T)^2 \left(\frac{h}{8f^2} - \frac{g^2}{12f^3} \right) . \quad (5.42)$$

We note that the last term in (5.39), if combined with F_{vib} , guarantees the correct dimension (erg) but is not important in the following and will be dropped. We now discuss the physical significance of the three remaining terms in (5.39). Φ_{el} represents the *static elastic energy* of the system; it is the sum of all interaction energies of the pairs of atoms at an equilibrium distance a apart. From (5.40) and (5.29a), we obtain explicitly

$$\Phi_{\text{el}}(\epsilon) = N \left[\varphi(a_0) + \frac{1}{2} f_0(a_0 \epsilon)^2 + \frac{1}{3!} g_0(a_0 \epsilon)^3 + \frac{1}{4!} h_0(a_0 \epsilon)^4 \right] . \quad (5.43)$$

Remember that a_0 is the lattice parameter of the undeformed chain and f_0 , g_0 , h_0 are the corresponding force constants while the deformation ϵ is defined by (5.24). The second term F_{vib} represents the *vibrational free energy* of the atoms; it is composed of a kinetic and a potential part. The third term F_{anh} contains the *specifically anharmonic effects* due to the vibration of the particles. It should be noted, however, that the anharmonicity is expressed not only in F_{anh} , but also manifests itself in Φ_{el} and F_{vib} by the altered lattice parameter a and the renormalized spring constant given by (5.29c), namely,

$$f(\epsilon) = f_0 + g_0 a_0 \epsilon + \frac{1}{2} h_0 (a_0 \epsilon)^2 . \quad (5.44)$$

In the harmonic approximation ($g = h = 0$), we have $F_{\text{anh}} = 0$, $f = f_0$ and the free energy is

$$F_h = \Phi_{\text{el},h} + F_{\text{vib},h} , \quad (5.45)$$

where

$$\Phi_{\text{el},h} = N \left[\varphi(a_0) + \frac{1}{2} f_0(a_0 \epsilon)^2 \right] \quad (5.46)$$

and

$$F_{\text{vib},h} = - \frac{N}{2} k_B T \left[\ln(2\pi m k_B T) + \ln \frac{2\pi k_B T}{f_0} \right] . \quad (5.47)$$

Note that F_{vib} and $F_{\text{vib},h}$ are formally identically; only the force constants are different.

5.2.3 The Equation of State and Thermal Expansion in the Quasiharmonic Approximation

For many applications, F_{anh} is neglected in (5.39); this represents the *quasiharmonic approximation* for which the free energy is defined by

$$F_{\text{qh}}(\epsilon) = \Phi_{\text{el}}(\epsilon) + F_{\text{vib}}(\epsilon) , \quad (5.48)$$

where $\Phi_{\text{el}}(\epsilon)$ is given by (5.43) and $F_{\text{vib}}(\epsilon)$ is given by (5.41,44).

From (5.17,24), we obtain for the force K acting on the chain

$$K = - \left(\frac{\partial F}{\partial L} \right)_T = - \frac{1}{L_0} \left(\frac{\partial F}{\partial \epsilon} \right)_T , \quad (5.49)$$

where $L_0 = N a_0$.

For the equation of state we find

$$K \simeq - \frac{1}{2} \frac{g_0}{f_0} k_B T - \left(f_0 + \frac{1}{2} \frac{h_0}{f_0} k_B T - \frac{1}{2} \frac{g_0^2}{f_0^2} k_B T \right) a_0 \epsilon - \frac{1}{2} g_0 a_0^2 \epsilon^2 . \quad (5.50)$$

Considering only linear terms in ϵ and neglecting terms proportional to h_0 and to g_0^2 , we find for the deformation

$$\epsilon(T, K) \simeq - \frac{1}{a_0 f_0} K - \frac{1}{2} \frac{g_0}{a_0 f_0^2} k_B T . \quad (5.51)$$

In the absence of an external force ($K = 0$), we obtain for the *thermal expansion*

$$\epsilon(T) = - \frac{1}{2} \frac{g_0}{a_0 f_0^2} k_B T . \quad (5.52)$$

$\epsilon(T)$ is normally positive since g_0 is negative. Equation (5.52) is completely equivalent to the expression (5.13) for the diatomic molecule. For the *coefficient of linear expansion*, we obtain from (5.52)

$$\alpha_L = \left(\frac{\partial \epsilon}{\partial T} \right)_K = - \frac{1}{2} \frac{g_0}{a_0 f_0^2} k_B . \quad (5.53)$$

The relations (5.52,53) can be written in a somewhat more general form, namely,

$$\epsilon(T) = - \frac{1}{2} \frac{g_0}{a_0 f_0^2} \bar{E}(T)/N , \quad (5.52a)$$

$$\alpha_L(T) = -\frac{1}{2} \frac{g_0}{a_0 f_0^2} c(T)/N . \quad (5.53a)$$

Here, $\bar{E}(T)/N$ and $c(T)/N$ are the mean thermal energy and specific heat per atom, respectively. In the classical case (high temperatures), $\bar{E}(T)/N = k_B T$ and $c(T)/N = k_B$. It can be shown that at low temperatures, the relations (5.52a,53a) are still valid if $\bar{E}(T)$ and $c(T)$ are replaced by the corresponding quantum mechanical expressions. According to (2.128), the mean vibrational energy is given by

$$\bar{E}(T) = \sum_s (\bar{n}_s + \frac{1}{2}) \hbar \omega_s .$$

Thus, even at $T = 0$, the thermal expansion ϵ given by (5.52a) is different from zero because of the zero-point energy.

We are now able to calculate the force constant f as a function of T and K . Neglecting terms proportional to ϵ^2 , we obtain from (5.44,51)

$$f(T,K) \approx f_0 - \frac{1}{2} \frac{g_0^2}{f_0^2} k_B T - \frac{g_0}{f_0} K . \quad (5.54)$$

We note that f decreases if T increases; furthermore, f increases for $K > 0$ (compression) and decreases for $K < 0$ (expansion) since $g_0 < 0$. For $K = 0$, we obtain

$$f(T) \approx f_0 - \frac{1}{2} \frac{g_0^2}{f_0^2} k_B T . \quad (5.55)$$

The eigenfrequencies of the harmonic chain are given by (2.43)

$$\omega_0^2(q_0) = 4 \frac{f_0}{m} \sin^2\left(\frac{q_0 a_0}{2}\right) . \quad (5.56)$$

In the quasiharmonic approximation, the phonons are still uncoupled but their frequencies are renormalized according to

$$\omega^2(q) = 4 \frac{f(T)}{m} \sin^2\left(\frac{qa}{2}\right) . \quad (5.57)$$

Note that since $q_0 = 2\pi m/Na_0$ and $q = 2\pi m/Na$, we have $q_0 a_0 = qa$. Substituting (5.55) in (5.57) yields

$$\omega^2(q,T) \approx \omega_0^2(q) \left[1 - \frac{1}{2} \frac{g_0^2}{f_0^3} k_B T \right] \quad (5.58a)$$

or

$$\omega(q, T) \simeq \omega_0(q) \left[1 - \frac{1}{4} \frac{g_0^2}{f_0^3} k_B T \right] . \quad (5.58b)$$

We define the *Grüneisen constant* $\gamma(q)$ of the linear chain by the following relation:

$$\frac{d\omega(q)}{\omega(q)} = - \gamma(q) \frac{dL}{L} . \quad (5.59a)$$

Thus, the relative change of the frequency is proportional to the relative change of the length $L = Na$, the constant of proportionality being the Grüneisen constant. The relation (5.59a) may be written in the form

$$\gamma(q) = - \frac{d \ln \omega(q)}{d \ln L} . \quad (5.59b)$$

Equation (5.59a) can be rewritten as

$$\gamma(q) = - \frac{a}{\omega(q)} \frac{d\omega(q)}{da} . \quad (5.59c)$$

Using the relations (5.24, 44, 57), one finds that

$$\gamma(q) \equiv \gamma = - \frac{1}{2} \frac{g_0}{f_0} a_0 . \quad (5.60)$$

Note that in our approximation, $\gamma > 0$ and is independent of q and T .

We define the "compressibility" κ_L of the linear chain by²

$$\kappa_L^{-1} = L \left(\frac{\partial^2 F}{\partial L^2} \right)_T = - L \left(\frac{\partial K}{\partial L} \right)_T = - (1 + \epsilon) \left(\frac{\partial K}{\partial \epsilon} \right)_T , \quad (5.61)$$

where for the last equation, we have used $L = L_0(1 + \epsilon)$. Using (5.50), we obtain

$$\kappa_L^{-1} = a_0 f_0 - \frac{1}{2} \left(\frac{g_0}{f_0} + 2a_0 \frac{g_0^2}{f_0^2} - a_0 \frac{h_0}{f_0} \right) k_B T . \quad (5.62)$$

In the harmonic approximation, $\kappa_{OL} = 1/a_0 f_0$ is independent of T . Neglecting terms proportional to h_0 , g_0^2 and ϵ^2 in (5.50) and using (5.60), we obtain

2 In three-dimensional systems, $\kappa^{-1} = V(\partial^2 F / \partial V^2)_T = - V(\partial P / \partial V)_T$. A linear system for which this definition can be applied consists of many parallel chains which are held together by rigid rods, such that corresponding atoms move in the same way. P is then the pressure which acts on the end surfaces and the equation of state becomes $PV_0 \simeq - (V - V_0)/\kappa_0 + \gamma N k_B T$.

for the equation of state

$$\kappa_{OL} L_0 \simeq - \frac{L - L_0}{\kappa_{OL}} + \gamma N k_B T . \quad (5.63)$$

5.2.4 The Specific Heat

Finally, we calculate the internal energy U and the specific heat c_L (at constant length) and c_K (at constant external force). For this purpose, we go beyond the quasiharmonic approximation by including the specific anharmonic term F_{anh} given by (5.42). From (5.18,39-42), we obtain

$$U \simeq N\varphi(a) + Nk_B T + N(k_B T)^2 \left(\frac{g_0^2}{12f_0^3} - \frac{h_0}{8f_0^2} \right) . \quad (5.64)$$

Here we have approximated F_{anh} (5.42) by replacing f , g and h by their unrenormalized values f_0 , g_0 , h_0 . From (5.19a), we find for the classical specific heat

$$c_L(T) \simeq Nk_B \left[1 + k_B T \left(\frac{g_0^2}{6f_0^3} - \frac{h_0}{4f_0^2} \right) \right] . \quad (5.65)$$

Thus, c_L normally increases linearly with T at high temperatures. From (5.19b,50,51), one finds

$$c_K - c_L \simeq \frac{1}{4} \frac{g_0^2}{f_0^3} N k_B^2 T \quad (5.66)$$

and using (5.53,62), we obtain

$$c_K - c_L = L_0 \frac{\alpha_L^2}{\kappa_{OL}} T . \quad (5.67)$$

5.3 The Anharmonic Three-Dimensional Crystal

5.3.1 The Equation of State

In the following, we consider an isotropic continuous medium. In this case, the free energy F depends only on the volume V and not on the individual coordinates of the atoms in the unit cell. For the equation of state, we can then write

$$P = - \left(\frac{\partial F}{\partial V} \right)_T . \quad (5.68)$$

[In the general anisotropic case, P has to be replaced by the components of the stress tensor and V by the components of the deformation tensor (Sect.3.6)]. We shall formulate the problem quantum mechanically but we often orientate ourselves by the results obtained for the classical linear chain. In particular, we use the quasiharmonic approximation, that is, we neglect the specific anharmonic term F_{anh} [see (5.42) for the linear chain]. Thus

$$F \approx F_{\text{qh}} = \Phi_{\text{el}}(a) + F_{\text{vib}}(\omega) . \quad (5.69)$$

Here the anharmonic nature appears only in the equilibrium distances a changed by thermal expansion, see (5.52), and the altered vibrational frequencies ω corresponding to the renormalized force constant f , see (5.55,57). We therefore approximate the atomic motion by a system of uncoupled normal vibrations but with different equilibrium positions and vibrational frequencies. This is, of course, an approximation since the anharmonic terms of the potential energy really lead to interactions of the normal vibrations. From (5.68,69), we obtain

$$P = - \frac{\partial \Phi_{\text{el}}}{\partial V} - \frac{\partial F_{\text{vib}}}{\partial V} . \quad (5.70)$$

As it is evident that the temperature is kept constant, the corresponding suffix will here and in the following be omitted. For the second term in (5.70) we write

$$\frac{\partial F_{\text{vib}}}{\partial V} = \sum_s \frac{F_{\text{vib}}}{\partial \omega_s} \frac{\partial \omega_s}{\partial V} . \quad (5.71)$$

In this expression s denotes the mode (j). In analogy to (5.59a), we define the Grüneisen parameter γ by

$$\frac{\partial \omega_s}{\partial V} = - \gamma_s \frac{\omega_s}{V} . \quad (5.72)$$

In Appendix N, we show that the free energy of the harmonic or quasiharmonic system is given by

$$F_{\text{vib}} = \frac{1}{2} \sum_s \hbar \omega_s + k_B T \sum_s \ln(1 - e^{-\hbar \omega_s / k_B T}) . \quad (5.73)$$

Differentiation of F_{vib} with respect to ω_s and using (2.126) and (5.72), we find for (5.71)

$$\frac{\partial F_{\text{vib}}}{\partial V} = - \frac{1}{V} \sum_s \gamma_s \bar{E}(\omega_s) , \quad (5.74)$$

where $\bar{E}(\omega_s)$ is the mean vibrational energy of the phonons s given by [see (2.127)],

$$\bar{E}(\omega_s) = (\bar{n}_s + \frac{1}{2}) \hbar \omega_s . \quad (5.75)$$

Using (5.70,74,75), the equation of state can be written in the form

$$\begin{aligned} P(V, T) &= - \frac{\partial \Phi_{\text{el}}}{\partial V} - \frac{\partial F_{\text{vib}}}{\partial V} \\ &= - \frac{\partial \Phi_{\text{el}}}{\partial V} + \frac{1}{V} \sum_s \gamma_s \left[\frac{1}{2} \hbar \omega_s + \frac{\hbar \omega_s}{\exp(\hbar \omega_s / k_B T) - 1} \right] . \end{aligned} \quad (5.76)$$

BOYER [5.15] recently presented a parameter-free calculation of the equation of state for KCl and NaCl based on (5.76). For this purpose he used the parameter-free pair potentials $\varphi(r)$ of GORDON and KIM [5.16]. It was then possible to calculate the dynamical matrix, ω_s , γ_s and Φ_{el} as a function of the internuclear distance r and hence of the volume V . Knowing these functions, it is then possible to derive $P(V, T)$ from (5.76). The result of this calculation for NaCl is shown in Fig.5.4 which gives the external pressure P as a function of the lattice parameter a for several temperatures. At room temperature and zero pressure, the calculation yields $a = 5.776 \text{ \AA}$, 2.6% larger than the observed value. With increasing pressure a decreases; on the other hand, for negative pressure (corresponding to a "hydrostatic tension"), a increases. For a given pressure, two values of a generally exist but only the smaller one is physically significant. If the temperature is increased at zero pressure, some critical temperature T_m exists above which $P(V, T)$ no longer intersects the $P = 0$ line. At this temperature, the crystal becomes unstable due to the vanishing of the isothermal bulk modulus $-V(dP/dV)_T$ at T_m . This lattice instability is consistent with melting. For NaCl, the calculation gives $T_m = 1130 \text{ K}$ in good agreement with the observed melting temperature of 1070 K.

For many applications it is permissible to simplify the equation of state (5.76) by using the fact that the changes in volume due thermal expansion are generally small. Φ_{el} and F_{vib} can, therefore, be expanded about the volume $V(T = 0)$ that the system has at $T = 0$. Neglecting the zero-point energy, we have $V(T = 0) = V_0$, where V_0 is the volume at which Φ_{el} has its minimum (see the corresponding discussion for the linear chain in Sect.4.1). Thus we write

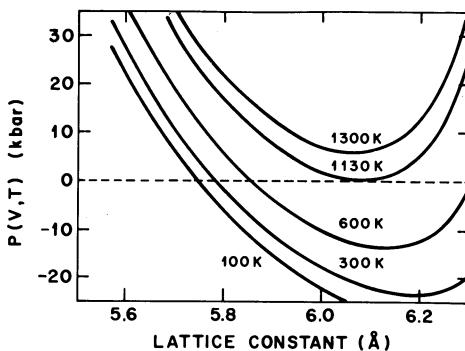


Fig. 5.4. External pressure $P(V,T)$ for NaCl as a function of lattice constant for several selected temperatures [5.15]

$$\Phi_{el} \approx \Phi_{el}(V_0) + \frac{1}{2} \left(\frac{\partial^2 \Phi_{el}}{\partial V^2} \right)_{V_0} (V - V_0)^2 , \quad (5.77)$$

$$F_{vib} \approx F_{vib}(V_0) + \left(\frac{\partial F_{vib}}{\partial V} \right)_{V_0} (V - V_0) . \quad (5.78)$$

From (5.77,78), we obtain

$$\frac{\partial \Phi_{el}}{\partial V} \approx \left(\frac{\partial^2 \Phi_{el}}{\partial V^2} \right)_{V_0} (V - V_0) , \quad (5.79)$$

$$\frac{\partial F_{vib}}{\partial V} \approx \left(\frac{\partial F_{vib}}{\partial V} \right)_{V_0} = - \frac{1}{V_0} \sum_s \gamma_s \bar{E}(\omega_{s0}) . \quad (5.80)$$

In the last equation of (5.80), we have used (5.74) and replaced V and ω_s by their values V_0 and ω_{s0} at $T = 0$. Equation (5.79) can be expressed in terms of the compressibility κ which is defined by (Sect. 5.2.3)

$$\kappa^{-1} = V \left(\frac{\partial^2 F}{\partial V^2} \right)_T . \quad (5.81)$$

At $T = 0$ and neglecting the zero-point energy, we find from (5.69)

$$\kappa_0^{-1} = V_0 \left(\frac{\partial^2 \Phi_{el}}{\partial V^2} \right)_{V_0} . \quad (5.82)$$

Making use of (5.79,80,82), we find for the equation of state (5.76)

$$PV_0 \approx - \frac{V - V_0}{\kappa_0} + \sum_s \gamma_s \bar{E}(\omega_{s0}) . \quad (5.83)$$

If γ is independent of s , we obtain

$$PV_0 \approx -\frac{V - V_0}{\kappa_0} + \gamma \bar{E}_{\text{vib}}(V_0) , \quad (5.84)$$

where $\bar{E}_{\text{vib}}(V_0)$ is the mean thermal energy at $V = V_0$. Equation (5.84) is the equation of state derived by Mie and Grüneisen. We note that in this approximation, the volume decreases linearly with increasing pressure. Note that (5.84) is completely analogous to the corresponding equation (5.63) for the linear chain.

5.3.2 Thermal Expansion

The thermal expansion can be derived from the equation of state; it is equal to the change in volume which the body undergoes without external pressure. Putting $P = 0$ in (5.83), we obtain for the thermal expansion $\epsilon = (V - V_0)/V_0$

$$\epsilon = \frac{\kappa_0}{V_0} \sum_s \gamma_s \bar{E}(\omega_{s0}) . \quad (5.85)$$

In analogy to (5.83), we obtain for the volume expansion coefficient

$$\alpha_V(T) = \left(\frac{\partial \epsilon}{\partial T} \right)_P = \frac{\kappa_0}{V_0} \sum_s \gamma_s c_{Vs}(T) , \quad (5.86)$$

where

$$c_{Vs}(T) = \frac{\partial \bar{E}(\omega_{s0})}{\partial T} \quad (5.87)$$

is the contribution of the mode s to the specific heat $c_V(T)$. At this point it is convenient to introduce an overall Grüneisen parameter

$$\bar{\gamma}(T) = \sum_s \gamma_s c_{Vs}(T) / c_V(T) \quad (5.88)$$

as the weighted average of the γ_s , in which the contribution of each mode is weighted by its contribution to the specific heat. Equation (5.88) implies that $\bar{\gamma}$ approaches a constant value as $T \rightarrow 0$ and a different constant value at high temperatures. Substituting (5.88) in (5.86) gives

$$\alpha_V(T) = \frac{\kappa_0}{V_0} \bar{\gamma}(T) c_V(T) . \quad (5.89)$$

Now assume that $\gamma_s = \gamma$, independent of the mode s ; in this case, $\bar{\gamma} = \gamma$ and we obtain

$$\alpha_V(T) = \frac{\kappa_0}{V_0} \gamma c_V(T) . \quad (5.90)$$

The relation (5.90) is known as the *Grüneisen relation*; it predicts that the volume expansion coefficient has the same temperature dependence as the specific heat. From (5.89,90) we see that the Grüneisen parameter characterizes the thermal expansion just as the Debye temperature characterizes the specific heat. The Grüneisen relation is approximately satisfied for many compounds with values of γ between 1 and 2.

An example of a model which gives a mode-independent Grüneisen parameter is the Debye approximation where $\omega_s = (q/q_D)\omega_D$. Using (5.72) and $k_{\omega_D} = k_B\theta_D$ (ω_D : Debye frequency, θ_D : Debye temperature), we obtain

$$\gamma_D = - \frac{V}{\omega_D} \frac{\partial \omega_D}{\partial V} = - \frac{V}{\theta_D} \frac{\partial \theta_D}{\partial V} = - \frac{\partial(\ln \theta_D)}{\partial(\ln V)} . \quad (5.91)$$

We now return to the general expression (5.89). If $\alpha_V(T)$, $c_V(T)$ and κ_0 are known from experiments, it is possible to obtain $\bar{\gamma}(T)$ (since κ is usually only weakly temperature dependent, κ_0 can often be replaced by κ). Figure 5.5 illustrates $\bar{\gamma}(T)$ for some selected compounds.

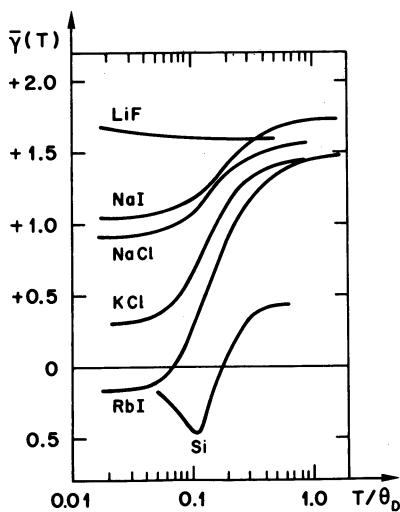


Fig. 5.5. Average Grüneisen parameter $\bar{\gamma}(T)$ vs T/θ_D for some alkali halide crystals [5.17] and for Si [5.18]

We note that for LiF, the mean Grüneisen parameter $\bar{\gamma}(T)$ is nearly temperature independent indicating that for this compound, the simple Grüneisen relation (5.90) is well satisfied. This is shown in Fig. 5.6 which illustrates

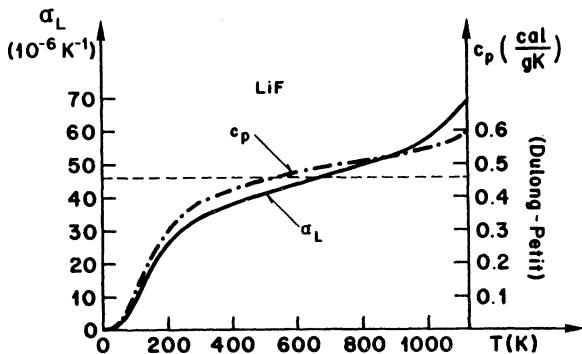


Fig. 5.6. Coefficient of thermal linear expansion α_L of LiF [5.19] and of the specific heat c_p [5.20] as a function of temperature

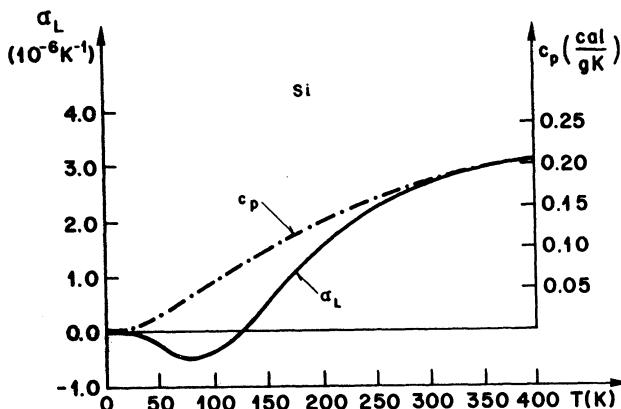


Fig. 5.7. Coefficient of thermal linear expansion α_L of Si [5.19] and of the specific heat c_p [5.21]

the coefficient of thermal linear expansion, $\alpha_L(T) = \alpha_V(T)/3$, together with $c_p(T)$ for LiF. For the other compounds shown in Fig. 5.5, however, $\bar{\gamma}(T)$ depends significantly on temperature, reflecting deviations from the Grüneisen relation (5.90). An extreme case is Si for which $\bar{\gamma}(T)$ is negative at low temperatures. The behaviour of $\alpha_L(T)$ and $c_p(T)$ are shown in Fig. 5.7. Heating up silicon from $T = 0$, it first contracts and expands only above ~ 125 K. Such behaviour seems to be typical for many compounds with tetrahedral coordination. Indeed, negative Grüneisen parameters and coefficients of thermal expansions have been found in ZnS, ZnSe, ZnTe [5.22], β -AgI [5.23], Cu₂O [5.24], as well as in Ge [5.25, 26].

We have already evaluated the Grüneisen parameter γ for the linear monoatomic chain with nearest neighbour interactions, (5.60), with the result that γ is proportional to the anharmonic force constant g of the cubic term in the potential energy (5.31, 32). If for a general three-dimensional crystal,

the anharmonic potential energy is written as

$$\sum_{\substack{\ell \ell' \ell'' \\ \kappa \kappa' \kappa'' \\ \alpha \beta \gamma}} \Phi_{\alpha \beta \gamma}(\ell \ell' \ell'') u_\alpha(\ell \kappa) u_\beta(\ell' \kappa') u_\gamma(\ell'' \kappa'') ,$$

it can be shown that the Grüneisen parameter of the mode (\vec{q}) with frequency $\omega_j(\vec{q})$ is given by [5.27,28]

$$\begin{aligned} \gamma_j(\vec{q}) = & - \frac{1}{2\omega_j(\vec{q})} \sum_{\substack{\ell \ell' \ell'' \\ \kappa \kappa' \kappa'' \\ \alpha \beta \gamma}} \Phi_{\alpha \beta \gamma}(\ell \ell' \ell'') r_\gamma(0 \ell \kappa'') \\ & \times e_\alpha(\kappa | \vec{q} | j) e_\beta(\kappa' | \vec{q} | j) e^{i \vec{q} \cdot \vec{r}(0 \ell \kappa')} . \end{aligned} \quad (5.92)$$

In this expression, $\vec{r}(0 \ell \kappa')$ is the vector joining the lattice points (0κ) and $(\ell \kappa')$ while $e_\alpha(\kappa | \vec{q} | j)$ are the components of the eigenvector $\vec{e}_j(\vec{q})$ of the harmonic problem. If the interatomic potential is known, as in the alkali-halides, or can be approximated by a $\varphi(r)$ involving a few parameters, the $\gamma_j(\vec{q})$ can be calculated from (5.92). In the case of Si, Ge, and diamond, the anharmonic potential energy was assumed to be a two-body force between nearest neighbours in which case the expression (5.92) is determined by two parameters. These two parameters were then adjusted to give reasonable agreement with the observed measured thermal expansion. The individual Grüneisen parameters $\gamma_s = \gamma_j(\vec{q})$ for the most symmetric directions are shown in Fig. 5.8 for Ge [5.27]. The results show that the values of the parameters γ_s differ markedly for the different normal modes, and that the short wavelength TA-modes have strongly negative Grüneisen parameters. Since in (5.88) γ_s is multiplied by $c_{VS}(T)$ which has a relatively large value for the acoustic modes at low temperatures, $\bar{\gamma}(T)$ and hence $\alpha_V(T)$ become negative below a certain temperature.

An example of a compound in which a negative Grüneisen parameter of an *optical* mode has been observed is β -AgI: in this crystal, a low-frequency Raman active mode at 17 cm^{-1} exists in which only the bond angles are changed [5.29]; this mode has a large negative pressure derivative and therefore a large negative gamma of $\sim 7.5!$ [5.30]. The associated negative coefficient of thermal expansion in this anisotropic crystal has recently been studied by HARVEY and FLETCHER [5.23]. General expressions for the coefficients of thermal expansion of anisotropic crystals were derived by LUDWIG [5.31].

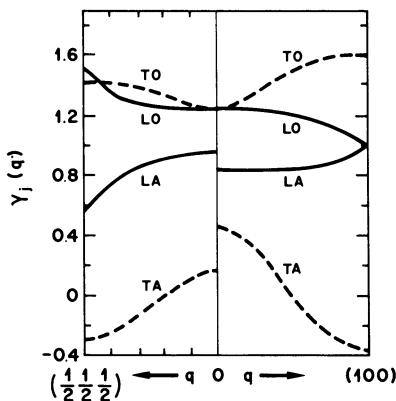


Fig.5.8. Calculated values of the Grüneisen parameter $\gamma_j(\vec{q})$ of Ge for \vec{q} parallel to (100) and (111) directions [5.27]

In Problem 5.6.4, the Grüneisen parameter for the $\vec{q} = 0$ optical modes of crystals with NaCl structure is evaluated on the basis of the Born-Mayer potential.

5.3.3 Anharmonic Effects on the Specific Heat and Elastic Constants

We have derived an expression for the specific heat of the anharmonic linear chain which is valid at high temperatures (5.65): due to anharmonicity, $c_L(T)$ is proportional to T at high temperatures. The same result also applies for the specific heat $c_V(T)$ of three-dimensional crystals [5.31,32]. As in (5.65), the coefficient of proportionality is determined by the third and fourth-order anharmonic coupling constants. In addition, the generalization of the expression (5.67) for $c_K - c_L$ to cubic crystals is straightforward, namely,

$$c_p - c_V = V_0 \frac{\alpha_V^2}{\kappa_0} T , \quad (5.93)$$

where α_V is the volume coefficient of expansion given by (5.89). Thus, at high temperatures, $c_p(T)$ is expected to be approximately proportional to T . An example is shown in Fig.5.6 for LiF. Above 500 K, c_p is approximately linear in T up to $T = 1000$ K. The deviation from the linear behaviour in the temperature range between 1000 K and 1120 K ($T_m = 1143$ K) is probably due to the formation of defects as well as to strong anharmonic effects.

In Sect.3.6, we established relations between the elastic constants and the atomic force constants (3.116,128,137). In Sect.5.2.2, we obtained the result that due to anharmonicity, the atomic force constants depend on temperature and pressure, (5.54,55). We therefore expect that the elastic con-

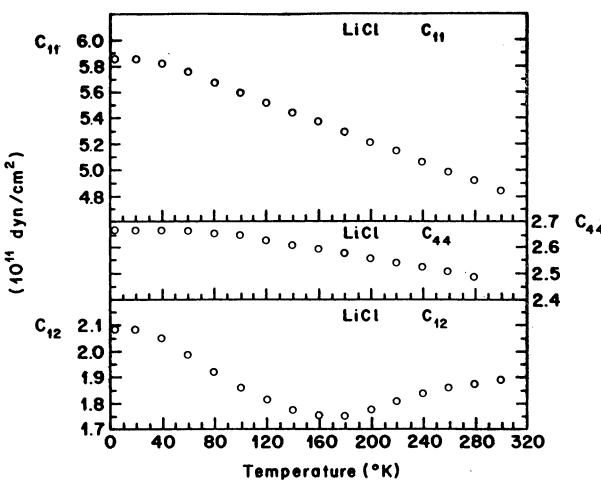


Fig. 5.9. Temperature dependence of the elastic constants (in units of 10^{11} dyn/cm^2) of LiCl [5.33]

stants also depend on temperature and pressure. This is born out by experiments. Figure 5.9 shows the temperature dependence of the elastic constants of LiCl [5.33].

5.4 The Self-Consistent Harmonic Approximation (SCHA)

5.4.1 General Remarks

The quasiharmonic approximation studied in Sects. 5.2,3 gives reasonable results for the thermodynamic properties of crystals in which the anharmonicity is weak and the force constants are renormalized by thermal expansion only. In crystals with very strong anharmonic interactions, however, this approximation breaks down. Examples are the vibrations in rare-gas solids, in particular solid helium, soft modes in ferro-electric phase transitions and melting processes. For these cases a method has been developed, the self-consistent harmonic approximation (SCHA), which allows a qualitative description of the effects of strong anharmonicity.

The SCHA has been the subject of many papers starting with the pionerring work of BORN [5.34] and HOOTON [5.35]. Subsequently, a number of important and independent studies have been performed, each in a different formalism: BOCCARA and SARMA [5.36], CHOQUARD [5.37], KOEHLER [5.38], HORNER [5.39], GILLIS et al. [5.40], and WERTHAMER [5.41].

The SCHA is based on the fact that if an atom in a crystal is executing oscillations of comparatively large amplitudes, it is not proper to treat

that motion in an approximation where the other atoms are held stationary. In the harmonic or quasiharmonic approximations, the restoring force acting on the atom ℓ if this atom is displaced from its equilibrium position, is calculated on the basis that all the other atoms are rigidly fixed to their lattice sites. [Remember that the force constant $\phi_{\alpha\alpha}(\ell\ell)$, for example, is the negative force acting on the atom ℓ in the direction α if this atom is displaced by a unit distance in this direction, while all the other atoms are held fixed; similarly, $\phi_{\alpha\beta}(\ell\ell')$ is the negative force exerted in the direction α on the atom ℓ when the atom ℓ' is displaced a unit distance in the direction β , while all the other atoms are kept at their equilibrium positions (Sect.3.1)]. *In contrast, the self-consistent phonon concept is that the forces on the atom of interest should rather be derived by regarding the other atoms as moving. This gives rise to the notion of an effective restoring force. It is defined as a thermodynamical average of the restoring force, taken over all configurations of the other atoms and weighted with the probability of each configuration.*

The SCHA is formally again harmonic, that is, the true lattice system is to be approximated by some other effective harmonic lattice whose force constants and lattice parameter are to be optimally adjusted. The renormalized force constants are obtained from a self-consistency condition. Self-consistency is achieved by replacing the normal harmonic force constants by effective force constants which are thermal averages with respect to the effective harmonic Hamiltonian.

In Sect.5.4.2, we demonstrate the basic physical principles with the help of the diatomic molecule. This is done in a rather intuitive way without any detailed derivations. In Sect.5.4.3, we discuss the SCHA for a Bravais crystal and in Sect.5.4.4, we treat the self-consistent Einstein model.

5.4.2 The Diatomic Molecule

Consider a diatomic molecule with a Morse-type potential of the form of (5.1), namely,

$$\varphi(R) = D(1 - e^{-\lambda(R - a_0)})^2 . \quad (5.94)$$

Here, a_0 is the distance at the minimum of $\varphi(R)$, D is the dissociation energy, λ is an adjustable parameter,

$$R = r + w \quad (5.95)$$

is the instantaneous separation, $r(T)$ is the mean separation at temperature T and $w = u_2 - u_1$ is the thermal fluctuation. The true Hamiltonian is

$$H = T_{\text{kin}} + \varphi(R) \quad (5.96)$$

and we define an effective harmonic Hamiltonian

$$\hat{H} = T_{\text{kin}} + \frac{1}{2} \hat{\phi} w^2 . \quad (5.97)$$

$\hat{\phi}$ is the effective force constant to be determined self-consistently. In the harmonic approximation, the equilibrium condition is

$$\left(\frac{\partial \varphi}{\partial R} \right)_{a_0} = 0 \quad (5.98)$$

and the force constant is defined by

$$\hat{\phi} = \left(\frac{\partial^2 \varphi}{\partial R^2} \right)_{a_0} . \quad (5.99)$$

The result of the SCHA (see Appendix 0) is physically appealing: the first and second derivatives of $\varphi(R)$ are simply replaced by their thermal averages with respect to the effective harmonic Hamiltonian \hat{H} . The equation which determines $r(T)$ at zero pressure is therefore

$$\left\langle \frac{\partial \varphi}{\partial R} \right\rangle_h = 0 , \quad (5.100)$$

while the effective force constant is given by

$$\hat{\phi} = \left\langle \frac{\partial^2 \varphi}{\partial R^2} \right\rangle_h . \quad (5.101)$$

In the classical case, the thermal average in (5.101) is defined by

$$\left\langle \frac{\partial^2 \varphi}{\partial R^2} \right\rangle_h = \frac{\int_{-\infty}^{+\infty} \frac{\partial^2 \varphi}{\partial R^2} \exp(-\frac{1}{2} \beta \hat{\phi} w^2) dw}{\int_{-\infty}^{+\infty} \exp(-\frac{1}{2} \beta \hat{\phi} w^2) dw} \quad (5.102)$$

and an analogous definition applies for (5.100). The index h means that the averages $\langle \dots \rangle_h$ are to be formed with respect to the effective harmonic Hamiltonian \hat{H} . Using the result

$$\int_{-\infty}^{+\infty} e^{-(ax^2+2bx+c)} dx = \left(\frac{\pi}{a}\right)^{\frac{1}{2}} \exp(b^2-ac)/a$$

one finds from (5.94,100)

$$r(T) = a_0 + \frac{3\lambda}{2\beta\hat{\phi}} = a_0 + \frac{3}{2} \frac{k_B T}{\hat{\phi}(T)} . \quad (5.103)$$

From (5.94,102), we find

$$\hat{\phi} = \phi \left[2 e^{-2\lambda(r-a_0)} e^{2\lambda^2/\beta\hat{\phi}} - e^{-\lambda(r-a_0)} e^{\lambda^2/2\beta\hat{\phi}} \right] , \quad (5.104)$$

where $\phi = 2D\lambda^2$ is the usual harmonic force constant, that is, the curvature of $\varphi(R)$ at $R = a_0$. This is a self-consistent equation for $\hat{\phi}$ if the mean interatomic distance is kept constant (this corresponds to constant volume in the three-dimensional case). For fixed r , we find from (5.104) that $\hat{\phi}$ increases with increasing temperature. This is understandable because with increasing temperature, the amplitude of vibration increases and the atoms feel the strong repulsive forces more and more. If we allow for thermal expansion ($P = \text{cst.} = 0$), we have to substitute (5.103) in (5.104) and obtain

$$\hat{\phi}(T) = \phi e^{-\lambda^2 k_B T / \hat{\phi}(T)} = \phi F(\hat{\phi}) . \quad (5.105)$$

Results similar to the relations (5.103,105) have been obtained for the self-consistent Einstein model of the linear chain [5.42]. For the molecule HCl, we have $D = 4.43$ ev, $\lambda^2 = 3.628 \times 10^{16} \text{ cm}^{-2}$ and $\phi = 5.15 \times 10^5 \text{ dyn/cm}$ [5.43]. Figure 5.10a shows the graphical solution of (5.105). The functions $\hat{\phi}(T)$ and $r(T)$ as obtained from (5.105) and (5.103) are illustrated in Fig. 5.10b.

Above the critical temperature $T_c = e^{-1} \phi / \lambda^2 k_B \approx 37800 \text{ K}$, (5.105) ceases to have a solution, indicating an instability of the molecule; this is also reflected in the slope of $r(T)$ which becomes infinite at T_c . The order of magnitude of T_c is roughly consistent with the dissociation temperature as derived from the dissociation energy D .

5.4.3 The SCHA for a Bravais Crystal

We start this section with the conventional lattice dynamics in the harmonic approximation. Using (3.27,29), the eigenvalue equation for a harmonic Bravais crystal has the form

$$\omega_j^2(\vec{q}) = \sum_{\alpha\beta} D_{\alpha\beta}(\vec{q}) e_\alpha^*(\vec{q}_j) e_\beta(\vec{q}_j) , \quad (5.106)$$

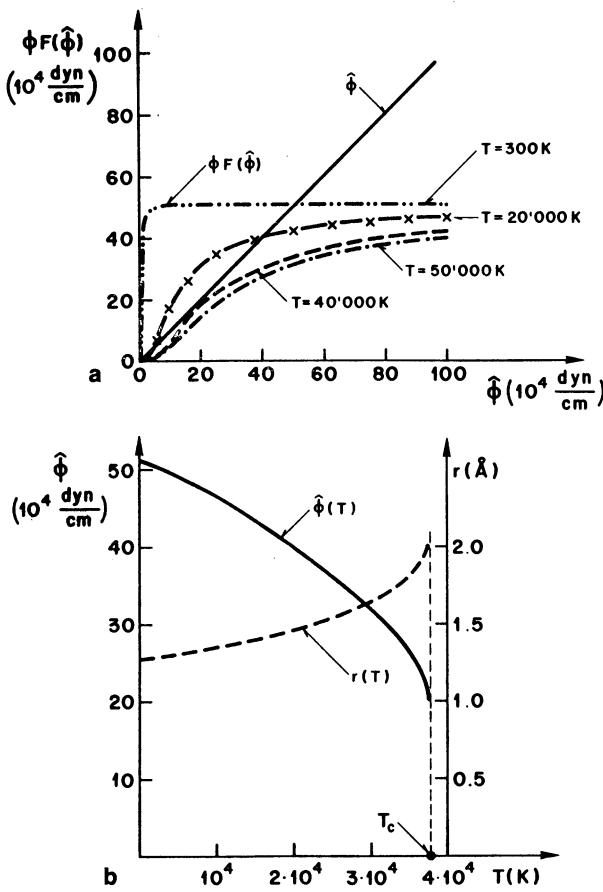


Fig. 5.10. a) Graphical solution of (5.105) for HCl. b) Temperature dependence of the force constant $\hat{\phi}$ and of the mean bond length r for HCl according to (5.105) and (5.103)

where according to (3.22), the dynamical matrix can be written as

$$D_{\alpha\beta}(\vec{q}) = \frac{1}{Nm} \sum_{\ell, \ell'} \Phi_{\alpha\beta}(\ell\ell') e^{i\vec{q}\vec{r}_{\ell\ell'}} .$$

Here, $\vec{r}_{\ell\ell'} = \vec{r}_{\ell'} - \vec{r}_\ell$. Using (3.17b), we obtain

$$D_{\alpha\beta}(\vec{q}) = \frac{1}{Nm} \sum'_{\ell, \ell'} \Phi_{\alpha\beta}(\ell\ell') (e^{i\vec{q}\vec{r}_{\ell\ell'}} - 1) . \quad (5.107)$$

The dash on the summation sign indicates that $\ell' \neq \ell$. In the following, we assume that the atoms interact pairwise by a potential $\varphi(R)$ which is a function only of the magnitude of the pair separation. According to (J.7) and (J.4), the force constants are then given by

$$\begin{aligned}\varphi_{\alpha\beta}(\ell\ell') &= -\varphi_{\alpha\beta}(\ell\ell') = -\left[\frac{\partial^2 \varphi(R_{\ell\ell'})}{\partial R_{\ell\ell'} \alpha \partial R_{\ell\ell'} \beta}\right]_h \\ &= -\left[\frac{\partial^2 \varphi(R_{\ell\ell'})}{\partial r_{\ell\ell'} \alpha \partial r_{\ell\ell'} \beta}\right]_h.\end{aligned}\quad (5.108)$$

Inserting (5.107,108) in (5.106), the eigenvalue equation assumes the form

$$\begin{aligned}m\omega_j^2(\vec{q}) \\ = \frac{1}{N} \sum'_{\ell\ell'} \sum_{\alpha\beta} e_\alpha^*(\vec{j}) e_\beta(\vec{j}) (1 - e^{i\vec{q}\vec{r}_{\ell\ell'}}) \varphi_{\alpha\beta}(\ell\ell') .\end{aligned}\quad (5.109)$$

Up to this point we have used conventional harmonic lattice dynamics. Introducing the density matrix [5.44] it is shown in Appendix 0 that in the SCHA, the harmonic force constants $\varphi_{\alpha\beta}(\ell\ell')$ are replaced by their thermal averages $\hat{\varphi}_{\alpha\beta}(\ell\ell'):$

$$\varphi_{\alpha\beta}(\ell\ell') \rightarrow \hat{\varphi}_{\alpha\beta}(\ell\ell') = \left\langle \frac{\partial^2 \varphi(R_{\ell\ell'})}{\partial r_{\ell\ell'} \alpha \partial r_{\ell\ell'} \beta} \right\rangle_h .\quad (5.110)$$

This leads to an eigenvalue equation which is formally identical to (5.109) but with effective frequencies $\hat{\omega}_j(\vec{q})$, effective eigenvectors $\hat{e}(\vec{j})$ and effective force constants $\hat{\varphi}_{\alpha\beta}(\ell\ell'):$

$$\begin{aligned}m\hat{\omega}_j^2(\vec{q}) \\ = \frac{1}{N} \sum'_{\ell\ell'} \sum_{\alpha\beta} \hat{e}_\alpha^*(\vec{j}) \hat{e}_\beta(\vec{j}) (1 - e^{i\vec{q}\vec{r}_{\ell\ell'}}) \hat{\varphi}_{\alpha\beta}(\ell\ell') .\end{aligned}\quad (5.109a)$$

At this point it is convenient to introduce the Fourier transform $\varphi(Q)$ of $\varphi(R):$

$$\varphi(Q) = \frac{1}{(2\pi)^3} \int d^3Q \varphi(Q) e^{i\vec{Q}\vec{R}} .\quad (5.111)$$

Putting

$$\vec{R}_{\ell\ell'} = \vec{r}_{\ell\ell'} + \vec{w}_{\ell\ell'} ,\quad (5.112)$$

where $\vec{r}_{\ell\ell'}$, is the mean separation and $\vec{w}_{\ell\ell'} = \vec{u}_{\ell'} - \vec{u}_\ell$, we obtain

$$\hat{\varphi}_{\alpha\beta}(\ell\ell') = -\frac{1}{(2\pi)^3} \int d^3Q Q_\alpha Q_\beta \varphi(Q) e^{i\vec{Q}\vec{r}_{\ell\ell'}} \langle e^{i\vec{Q}\vec{w}_{\ell\ell'}} \rangle_h .\quad (5.113)$$

We now use the result that for harmonic oscillators, the thermal average appearing in (5.113) is given by

$$\langle e^{i\vec{Q}\vec{w}_{\ell\ell'}} \rangle_h = e^{-D_{\ell\ell'}(\vec{Q})} , \quad (5.114)$$

where

$$D_{\ell\ell'}(\vec{Q}) = \frac{1}{2} \langle (\vec{Q}\vec{w}_{\ell\ell'})^2 \rangle_h . \quad (5.115)$$

This result can be roughly justified by expanding both sides of (5.114) in a Taylor series and noting that $\langle \vec{Q}\vec{w}_{\ell\ell'} \rangle_h = \langle (\vec{Q}\vec{w}_{\ell\ell'})^3 \rangle_h = \dots = 0$. A full proof of the above result can be found in [5.45]. Substituting (5.113,114) in (5.109a), we find

$$\begin{aligned} m\hat{\omega}_j^2(\vec{q}) &= -\frac{1}{(2\pi)^3} \int d^3Q |\hat{Q}\hat{e}_j(\vec{q})|^2 \varphi(Q) \\ &\times \sum'_{\ell'} (1 - e^{i\vec{q}\vec{r}_{\ell\ell'}}) e^{i\vec{Q}\vec{r}_{\ell\ell'}} e^{-D_{\ell\ell'}(\vec{Q})} . \end{aligned} \quad (5.116)$$

In Appendix 0 we show that

$$\begin{aligned} D_{\ell\ell'}(Q) &= \frac{\mu}{2Nm} \sum_{\vec{q}j} \frac{|\hat{Q}\hat{e}_j(\vec{q})|^2}{\hat{\omega}_j(\vec{q})} (1 - e^{i\vec{q}\vec{r}_{\ell\ell'}}) \coth \frac{\hbar\omega_j(\vec{q})}{2k_B T} \\ &= \frac{1}{Nm} \sum_{\vec{q}j} |\hat{Q}\hat{e}_j(\vec{q})|^2 \frac{\hat{E}_j(\vec{q})}{\hat{\omega}_j^2(\vec{q})} [1 - \cos(\vec{q}\vec{r}_{\ell\ell'})] . \end{aligned} \quad (5.117)$$

Once the pair potential $\varphi(R)$ is given its Fourier transform, $\varphi(Q)$ can be calculated and from (5.116,117), the effective harmonic frequencies $\hat{\omega}_j(\vec{q})$ and the eigenvectors $\hat{e}_j(\vec{q})$ can be determined self-consistently for a fixed choice of crystal structure and lattice spacings. This corresponds to a crystal with constant volume. Equation (5.116) together with (5.117) correspond to (5.104) for the diatomic molecule. In Appendix 0, it is shown that the self-consistent equation of state for cubic crystals is given by (0.26), namely,

$$PV = -\frac{1}{2} N \sum_{\ell} \vec{r}_{0\ell} \langle \nabla \varphi(\vec{r}_{0\ell} + \vec{w}_{0\ell}) \rangle_h . \quad (5.118)$$

Putting $P = 0$, we obtain the self-consistent equilibrium condition at zero pressure:

$$\sum'_{\ell} \vec{r}_{0\ell} \langle \nabla \varphi(\vec{r}_{0\ell} + \vec{w}_{0\ell}) \rangle_h = 0 . \quad (5.119)$$

In these equations, $\vec{r}_{0\ell} = (r_{0\ell x}, r_{0\ell y}, r_{0\ell z})$ defines the equilibrium position of atom ℓ with respect to the atom 0 at the origin and $\nabla = (\partial/\partial r_{0\ell x}, \partial/\partial r_{0\ell y}, \partial/\partial r_{0\ell z})$,

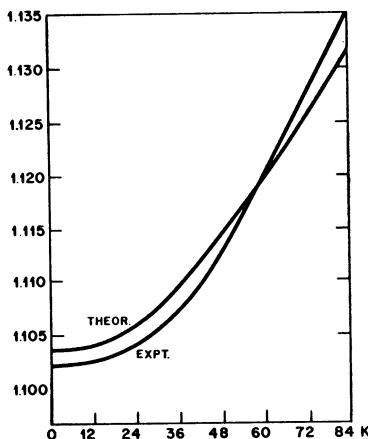


Fig. 5.11. Nearest-neighbour distance in units of $\sigma=3.407 \text{ \AA}$ for argon at zero pressure vs temperature [5.40]

$\partial/\partial r_{0\ell z}$). The relation (5.119) corresponds to the condition (5.100) for the diatomic molecule. When (5.109a) or (5.116,117) are solved together with (5.119), we are evaluating the self-consistent frequencies and eigenvectors at constant pressure; this corresponds to the relation (5.105) for the diatomic molecule.

The SCHA as described by the relations (5.116-119) has been applied to compute the self-consistent phonon frequencies, thermal expansion, compressibility and specific heat of Argon and Neon [5.40]. Figure 5.11 shows the thermal expansion of Argon; the calculation is based on the Lennard-Jones 6-12 potential (4.2).

5.4.4 The Self-Consistent Isotropic Einstein Model

In order to illustrate the SCHA, we consider the simplest possible model, the self-consistent isotropic Einstein model [5.46]. In the Einstein model, each atom is bound by a spring with force constant ϕ to its equilibrium position. Starting from the general relation (3.12), we disregard all coupling coefficients other than the diagonal term $\phi_{\alpha\alpha}(00)$ and write for the force acting on the atom 0 in the direction α

$$F_\alpha(0) = m\ddot{u}_\alpha(0) = -\phi_{\alpha\alpha}(00)u_\alpha(0) .$$

In a real crystal, the force constant $\phi = \phi_{\alpha\alpha}(00)$ is, of course, due to the interactions of atom 0 with its neighbouring atoms ℓ , and this is expressed by the relation (3.17b) which gives

$$\phi = m\omega^2 = -\sum_\ell' \phi_{\alpha\alpha}(0\ell) ,$$

where the dash on the summation sign means that $\ell \neq 0$. If the atoms interact pairwise by a pair potential $\varphi(R)$, we use (J.7) and in the SCHA, ϕ is replaced by the effective force constant

$$\hat{\phi} = \frac{1}{3} \sum_{\alpha} \sum'_{\ell} \left\langle \frac{\partial^2 \varphi(R_{0\ell})}{\partial R_{0\ell\alpha}^2} \right\rangle_h . \quad (5.120)$$

Introducing the Fourier transform $\varphi(Q)$ of $\varphi(R)$ by

$$\varphi(R) = \frac{1}{(2\pi)^3} \int d^3Q \varphi(Q) e^{i\vec{Q}\cdot\vec{R}} , \quad (5.121)$$

(5.120) can be written in the form

$$\hat{\phi} = -\frac{1}{3} (2\pi)^{-3} \int d^3Q Q^2 \varphi(Q) \sum'_{\ell} e^{i\vec{Q}\cdot\vec{r}_{0\ell}} \langle e^{i\vec{Q}\cdot\vec{w}_{0\ell}} \rangle_h . \quad (5.122)$$

Here, $\vec{R}_{0\ell} = \vec{r}_{0\ell} + \vec{w}_{0\ell}$ where $\vec{r}_{0\ell}$ are the equilibrium positions and $\vec{w}_{0\ell} = \vec{u}_\ell - \vec{u}_0$ are the relative displacements. Applying (5.114,115) and using the fact that in the Einstein model there is no cross-correlation, that is, $\langle \vec{u}_0 \cdot \vec{u}_\ell \rangle_h = 0$ for $\ell \neq 0$, and observing that at high temperatures $\langle u_{\ell\alpha}^2 \rangle_h = k_B T / \hat{\phi}$, we obtain

$$\hat{\phi} = -\frac{1}{3} (2\pi)^{-3} \int d^3Q Q^2 \varphi(Q) e^{-Q^2 k_B T / \hat{\phi}} \sum'_{\ell} e^{i\vec{Q}\cdot\vec{r}_{0\ell}} . \quad (5.123)$$

From

$$\sum'_{\ell} e^{i\vec{Q}\cdot\vec{r}_{0\ell}} = \frac{(2\pi)^3}{V_a} \sum_{\vec{\tau}} \delta(\vec{Q} - \vec{\tau}) - 1 , \quad (5.124)$$

we obtain

$$\hat{\phi} = \hat{\phi}_1 + \hat{\phi}_2 , \quad (5.125)$$

where

$$\hat{\phi}_1 = \frac{1}{3} (2\pi)^{-3} \int d^3Q Q^2 \varphi(Q) e^{-Q^2 k_B T / \hat{\phi}} \quad (5.126)$$

and

$$\hat{\phi}_2 = -\frac{1}{3V_a} \sum_{\vec{\tau}} \tau^2 \varphi(\tau) e^{-\tau^2 k_B T / \hat{\phi}} . \quad (5.127)$$

In order to avoid computational difficulties, we choose as the interatomic potential a simple form of Gaussian type [5.46], namely,

$$\varphi(R) = Ae^{-uR^2} - Be^{-vR^2} . \quad (5.128)$$

From

$$\int d^3R e^{-pR^2} e^{-i\vec{Q}\vec{R}} = (\frac{\pi}{p})^{3/2} e^{-Q^2/4p},$$

we obtain

$$\varphi(Q) = (2\pi)^3 (\Gamma e^{-\xi Q^2} - \Lambda e^{-\eta Q^2}), \quad (5.129)$$

where

$$\Gamma = A(4\pi u)^{-3/2}, \quad \Lambda = B(4\pi v)^{-3/2},$$

$$\xi = 1/4u, \quad \eta = 1/4v. \quad (5.130)$$

Substituting (5.129) in (5.125-127), we obtain the result

$$\begin{aligned} \hat{\phi} &= (\pi^{3/2}/2) \left[\Gamma \left(\xi + \frac{k_B T}{\hat{\phi}} \right)^{-5/2} - \Lambda \left(\eta + \frac{k_B T}{\hat{\phi}} \right)^{-5/2} \right] \\ &\quad - \frac{(2\pi)^3}{3V_a} \sum_{\tau} \tau^2 [\Gamma e^{-\tau^2(\xi+k_B T/\hat{\phi})} - \Lambda e^{-\tau^2(\eta+k_B T/\hat{\phi})}]. \end{aligned} \quad (5.131)$$

This is an explicit self-consistent equation for the force constant $\hat{\phi}$ for a given crystal structure and lattice spacing ($V = \text{constant}$). For silver (fcc lattice with lattice parameter $a = 4.08 \text{ \AA}$ at 300 K), the parameters in (5.128) have the following values [5.46]: $A = 69.27 \text{ eV}$, $B = 1.612 \text{ eV}$, $u = 0.6922 \text{ \AA}^{-2}$, $v = 0.1395 \text{ \AA}^{-2}$. This gives $\Gamma = 4.325 \times 10^{-36} \text{ dyn cm}^4$, $\Lambda = 1.112 \times 10^{-36} \text{ dyn cm}^4$, $\xi = 36.12 \times 10^{-18} \text{ cm}^2$, $\eta = 179.2 \times 10^{-18} \text{ cm}^2$ and $V_a = 16.98 \times 10^{-24} \text{ cm}^3$. Solving (5.131) for $\hat{\phi}$, we obtain $\hat{\phi} = 1.8 \times 10^5 \text{ dyn/cm}$ at 300 K. A calculation based on the harmonic approximation and nearest-neighbour interactions gives $\phi = 2.0 \times 10^5 \text{ dyn/cm}$. From (5.131), it can be verified that $\hat{\phi}$ increases with increasing temperature just as for the diatomic molecule with fixed bond length (5.104); this corresponds to the crystal at constant volume ("clamped" crystal). If we allow for thermal expansion via (5.119), we are calculating $\hat{\phi}$ at constant pressure and in this case, $\hat{\phi}$ decreases with increasing temperature.

5.5 Response Function and Perturbation Theory of Phonon-Phonon Interactions

In this section, we first consider the response of a system to an external perturbation; this leads to the important concept of the *response function*. As an illustration, we discuss the response of a system of harmonic and damped harmonic oscillators to an external electric field. We then discuss

the response function of a crystal with weakly interacting phonons. This response function depends on renormalized phonon frequencies which can be calculated by perturbation theory, regarding the anharmonic part of the Hamiltonian as a weak perturbation. The discussion in this section is qualitative, no detailed derivations are given. The most elegant method is based on Green's function techniques and the interested reader is referred to the literature [Ref.2.11,p.181].

5.5.1 Response Function of Harmonic and Damped Harmonic Oscillators

In Sect.4.3.2, we considered the dielectric constant for a multi-atomic crystal. The result can be written in the form, see (4.115),

$$\epsilon(\omega) - \epsilon_{\infty} = \sum_j \frac{S_j}{\omega_j^2(0) - \omega^2} , \quad (5.132)$$

where S_j is the oscillator strength and $\omega_j(0)$ is the harmonic frequency of the j^{th} transverse optical mode at $\vec{q} = 0$. $\epsilon(\omega)$ represents the response of the crystal to an external perturbation, namely, a transverse electric field of the form $\vec{E} = \vec{E}_0 \exp[i(\vec{k}\vec{r} - \omega t)]$ for which $\vec{k} = 0$. We therefore define a response function for each mode by

$$R_j(\vec{q} = 0, \omega) = [\omega_j^2(0) - \omega^2]^{-1} , \quad (5.133)$$

in terms of which, (5.132) can be written as

$$\epsilon(\omega) - \epsilon_{\infty} = \sum_j S_j R_j(0, \omega) . \quad (5.134)$$

Next consider a system of damped simple harmonic oscillators with frequencies $\omega_j(0)$ and damping constants $\Gamma_j(0)$. The equation of motion of the normal coordinate Q_j is then

$$\ddot{Q}_j + 2\Gamma_j \dot{Q}_j + \omega_j^2 Q_j = f_j^{1/2} E_0 e^{-i\omega t} \quad (5.135)$$

(the factor 2 in the damping term is traditional). Equation (5.135) can be derived from phenomenological equations of motion in which the total force acting on each ion of the crystal is composed of a harmonic force, a friction force and a driving force due to the applied electric field $E_0 \exp(-i\omega t)$ (Problem 5.6.6).

It is then easily shown (Problem 5.6.6) that the dielectric constant can be written in the form

$$\epsilon(\omega) - \epsilon_{\infty} = \sum_j S_j R_j(0, \omega) , \quad (5.136)$$

where $S_j = (4\pi/v_a)f_j$ and the response function is given by

$$R_j(0, \omega) = [\omega_j^2(0) - \omega^2 - 2i\Gamma_j(0)\omega]^{-1} . \quad (5.137)$$

Figure 5.12 shows the real and imaginary part of $R_j(0, \omega)$.

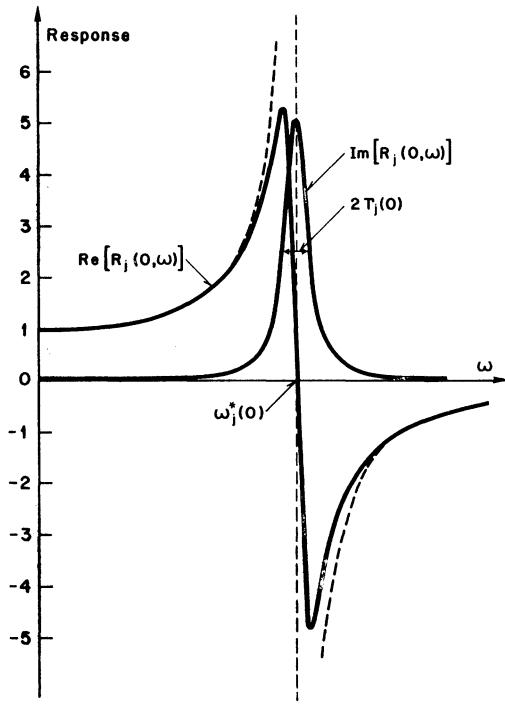


Fig. 5.12. Real and imaginary parts of the response function $R_j(0, \omega)$ of a damped harmonic oscillator. We have chosen $\Gamma_j(0)/\omega_j(0)=0.05$. For the harmonic oscillator $\Gamma_j(0)=0$; for this case, $\text{Re}\{R_j(0, \omega)\}$ is shown by the dashed line and $\text{Im}\{R_j(0, \omega)\}$ is a delta function centered at $\omega=\omega_j(0)$. $\omega_j(0) \approx [\omega_j^2(0) - \Gamma_j^2(0)]^{1/2}$

The imaginary part of $R_j(0, \omega)$ has a peak at the frequency $\omega_j^*(0) \approx [\omega_j^2(0) - \Gamma_j^2(0)]^{1/2}$ and of width $2\Gamma_j(0)$. The harmonic oscillator is obtained in the limit $\Gamma_j(0) \rightarrow 0$. The real part of $R_j(0, \omega)$ is then given by (5.133), while the imaginary part of $R_j(0, \omega)$ degenerates to a delta function centered at $\omega = \omega_j(0)$ (Fig. 5.12).

The response function can be generalized for any mode not necessarily having $\vec{q} = 0$; in the present approximation, we define

$$R_j(\vec{q}, \omega) = [\omega_j^2(\vec{q}) - \omega^2 - 2i\Gamma_j(\vec{q})\omega]^{-1} . \quad (5.138)$$

This is the response function of a damped harmonic oscillator resonating at the frequency $\omega_j(\vec{q})$ and having a peak width of $2\Gamma_j(\vec{q})$. Such response functions appear not only in the dielectric constant which can be studied by

infrared absorption experiments, but also in light scattering and inelastic neutron scattering experiments [1.35].

5.5.2 Response Function for the Anharmonic Crystal

Up to now we have considered the response function for a system of damped harmonic oscillators. If we allow for anharmonic interactions between phonons, the response function will be modified. The theory of crystal dynamics in which anharmonic effects are weak gives the following expression for the response function [5.47]

$$R_j(\vec{q}, \omega) = [\omega_j^2(\vec{q}) - \omega^2 + 2\omega_j(\vec{q}) \sum_j(\vec{q}, \omega)]^{-1} . \quad (5.139)$$

In this expression, $\omega_j(\vec{q})$ is the harmonic frequency of the mode (j) and $\sum_j(\vec{q}, \omega)$ is known as the (complex) "self-energy" of this mode and is given by

$$\sum_j(\vec{q}, \omega) = \Delta_j(\vec{q}, \omega) - i\Gamma_j(\vec{q}, \omega) . \quad (5.140)$$

Since we assume that $\Delta_j(\vec{q}, \omega)$ and $\Gamma_j(\vec{q}, \omega)$ are small compared with $\omega_j(\vec{q})$, the expression (5.139) can also be written in the form

$$R_j(\vec{q}, \omega) \simeq \left\{ [\omega_j(\vec{q}) + \sum_j(\vec{q}, \omega)]^2 - \omega^2 \right\}^{-1} . \quad (5.141)$$

From this expression it is obvious that due to anharmonic interactions, each harmonic frequency $\omega_j(\vec{q})$ is replaced by a complex frequency

$$\Omega_j(\vec{q}, \omega) = \omega_j(\vec{q}) + \sum_j(\vec{q}, \omega) . \quad (5.142)$$

It therefore follows that the normal coordinate of the harmonic mode, $Q_j(q) \sim \exp[-i\omega_j(\vec{q})t]$, is now replaced by a normal coordinate with a time variation $Q_j \sim \exp[-i\Omega_j(\vec{q}, \omega)t]$, or

$$Q_j(\vec{q}) \sim e^{-i[\omega_j(\vec{q}) + \Delta_j(\vec{q}, \omega)]t} e^{-\Gamma_j(\vec{q}, \omega)t} . \quad (5.143)$$

Thus the effective frequency of the mode is $\omega_j(\vec{q}) + \Delta_j(\vec{q}, \omega)$ and the damping constant is $\Gamma_j(\vec{q}, \omega)$. Both the shift and the damping constant depend on the frequency ω with which the crystal is "probed". We shall see later that $\Gamma_j(\vec{q}, \omega)$ and $\Delta_j(\vec{q}, \omega)$ also depend on temperature. In the presence of anharmonic interactions, the dielectric constant is still given by the relation (5.136) but with $R_j(0, \omega)$ now given by (5.141).

From (5.141) it is easily seen that a resonance in the response function and a peak in its imaginary part will be determined by the condition

$$\omega^2 = \omega_j^2(\vec{q}) + 2\omega_j(\vec{q})\Delta_j(\vec{q}, \omega) . \quad (5.144)$$

Let $\tilde{\omega}_j(\vec{q})$ be the *pseudoharmonic frequency* satisfying this condition and $\tilde{\Gamma}_j(\vec{q})$ be $\Gamma_j(\vec{q}, \omega)$ evaluated at $\omega = \tilde{\omega}_j(\vec{q})$. Then it is often a reasonable approximation, at least in the neighbourhood of the resonances of the response function, to write

$$R_j(\vec{q}, \omega) = [\tilde{\omega}_j^2(\vec{q}) - \omega^2 - 2i\tilde{\Gamma}_j(\vec{q})\omega]^{-1} . \quad (5.145)$$

This approximate expression is similar to the response function (5.138) which we wrote down by analogy with the expressions (5.136,137) for $\epsilon(\omega)$, except that the harmonic frequency $\omega_j(\vec{q})$ has been replaced by the pseudo-harmonic frequency $\tilde{\omega}_j(\vec{q})$ and $\Gamma_j(\vec{q})$ has been replaced by $\tilde{\Gamma}_j(\vec{q})$. From the experimental point of view, we see that $\tilde{\omega}_j(\vec{q})$ and $\tilde{\Gamma}_j(\vec{q})$ are to be determined from the measured positions and half-widths of the infrared absorption bands, the Raman lines, or the peaks of inelastic neutron scattering spectra. Examples of infrared experimental data are shown in Fig.5.14. The pseudo-harmonic frequencies $\tilde{\omega}_j(\vec{q})$ defined by (5.144) should not be confused with the quasiharmonic frequencies discussed in Sects.5.2,3. In the latter, the change in frequencies with temperature is due only to thermal expansion. The pseudoharmonic frequencies, however, are not only effected by thermal expansion but also by interactions of the phonon (\vec{q}_j) with other phonons. This will be discussed below.

5.5.3 Frequency Widths and Shifts from Perturbation Theory

It remains to calculate $\Gamma_j(\vec{q}, \omega)$ and $\Delta_j(\vec{q}, \omega)$ which appear in the response function (5.141). We start from the Hamiltonian $H = H_0 + H'$, where H_0 is the harmonic part given by (3.71) and H' is the anharmonic part taken to be

$$H' = H_3 + H_4 . \quad (5.146)$$

H_3 and H_4 describe the cubic and quartic anharmonic interactions; higher-order terms are neglected in the Taylor expansion of the potential energy. H' is given by

$$H' = \frac{1}{3!} \sum_{ijk} \Phi_{ijk} u_i u_j u_k + \frac{1}{4!} \sum_{ijkl} \Phi_{ijkl} u_i u_j u_k u_l , \quad (5.147)$$

where we have used the abbreviations $i = (\ell\kappa\alpha)$, etc. Using (3.74), which expresses the displacement coordinates in terms of creation and annihilation operators a_{-s}^+ and a_s , respectively, where s stands for (\vec{q}, j) and $-s$ for $(-\vec{q}, j)$, and putting

$$A_s = a_{-s}^+ + a_s, \quad (5.148)$$

we show in Appendix P that H' can be written in the form

$$\begin{aligned} H' = & \sum_{ss_1 s_2} V(s, s_1, s_2) A_s A_{s_1} A_{s_2} \\ & + \sum_{ss_1} \sum_{s_2 s_3} V(s, s_1, s_2, s_3) A_s A_{s_1} A_{s_2} A_{s_3}. \end{aligned} \quad (5.149)$$

In this expression, $s_i = (\vec{q}_i, j_i)$. The coefficients $V(\dots)$ are complicated functions of the eigenfrequencies, eigenvectors, anharmonic coupling coefficients and atomic masses, and are given in Appendix P. Due to translational invariance of the potential energy, the wave vectors \vec{q}_i in (5.149) obey momentum conservation, that is,

$$\vec{q} + \vec{q}_1 + \vec{q}_2 = \vec{\tau} \quad (5.150a)$$

for H_3 and

$$\vec{q} + \vec{q}_1 + \vec{q}_2 + \vec{q}_3 = \vec{\tau} \quad (5.150b)$$

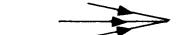
for H_4 , where $\vec{\tau}$ is any reciprocal lattice vector including zero. The operator H_3 describes three-phonon interactions, while the operator H_4 describes four-phonon processes. This can be seen by writing out the product $A_s A_{s_1} A_{s_2}$ using (5.148); one obtains the following eight terms:

$$\begin{aligned} & a_s a_{-s_1}^+ a_{-s_2}^+ + a_s a_{s_1}^+ a_{-s_2}^+ + a_s a_{-s_1}^+ a_{s_2}^+ + a_s a_{s_1}^+ a_{s_2}^+ \\ & + a_{-s}^+ a_{s_1}^+ a_{s_2}^+ + a_{-s}^+ a_{-s_1}^+ a_{s_2}^+ + a_{-s}^+ a_{s_1}^+ a_{-s_2}^+ + a_{-s}^+ a_{-s_1}^+ a_{-s_2}^+. \end{aligned} \quad (5.151)$$

In this list, term 1, for example, is an operator which acts on the complete phonon state $| \dots \rangle$ to give a reduction of unity in the occupation number for the mode (\vec{q}, j) and an increase of unity in each of the phonons (\vec{q}_1, j_1) and (\vec{q}_2, j_2) . In other words, one phonon splits into two. The complete classification is given in Table 5.1.

From Table 5.1, it follows that there are four basic processes: (i) absorption of a phonon with the creation of two other phonons, (ii) absorption of two phonons with the creation of another, (iii) simultaneous disappearance

Table 5.1. Schematic representation of the eight three-phonon processes described by H_3 and listed in (5.151). Note that positive \vec{q} 's appear as convergent and negative \vec{q} 's as divergent vectors

Term number in (5.151)	Creation	Annihilation	Representation
1,6,7	2	1	
2,3,5	1	2	
4	0	3	
8	3	0	

of three phonons, and (iv) simultaneous creation of three phonons. Possibilities (iii), (iv) clearly violate energy conservation. For the calculation of the lifetime of a phonon, we must, however, include them as possible virtual subprocesses in multiple step interactions. All these processes must be considered in the light of (5.150), remembering that the \vec{q} 's are restricted to the first Brillouin zone. Processes with $\vec{\tau} = 0$ are known as normal or *N-processes*, those with $\vec{\tau} \neq 0$ are known as "Umklapp" or *U-processes*.

The lifetime $\tau_j(\vec{q})$ of the phonon $(\vec{q}j)$ is defined as the reciprocal value of the probability that a phonon $(\vec{q}j)$ will vanish as a result of the processes shown in Table 5.1. This probability is the sum of the probabilities for the processes in which phonons $(\vec{q}j)$ are destroyed, minus the sum of the probabilities for those processes by which phonons $(\vec{q}j)$ are created.

According to the "golden rule" of perturbation theory [Ref.2.9,p.285], the partial transition probability for the process described by the first term in (5.151), for example, is given by

$$\frac{2\pi}{\hbar} |V(s, -s_1, -s_2)|^2 |\langle f | a_s a_{-s_1}^+ a_{-s_2}^+ | i \rangle|^2 \delta(E_f - E_i) , \quad (5.152)$$

where $|i\rangle$ denotes the initial state with energy E_i and $|f\rangle$ the final state with energy E_f . The delta function signifies conservation of energy. The four-phonon processes described by H_4 do not contribute to $\tau_j(\vec{q})$. The reciprocal of $\tau_j(\vec{q})$ calculated by this procedure is identical to the value of the damping function $\Gamma_j(\vec{q}, \omega)$ evaluated at $\omega = \omega_j(\vec{q})$. It is, in principle, also possible to obtain the contributions of H_3 and H_4 to the frequency shift $\Delta_j(\vec{q}, \omega)$ at $\omega = \omega_j(\vec{q})$ by applying standard perturbation theory. The

contributions of H_4 are first-order terms and those of H_3 are second-order terms [5.48]. In addition, there is a contribution to $\Delta_j(\vec{q}, \omega)$ which is due to thermal expansion and which we considered in detail in Sect.5.3 on the basis of the quasiharmonic approximation. Inevitably, the calculations based on standard perturbation theory are complicated and cumbersome; it is more convenient to calculate both $\Delta_j(\vec{q}, \omega)$ and $\Gamma_j(\vec{q}, \omega)$ by using Green's function techniques [Ref.2.11,p.181]. For later discussions we quote the final results. For the damping function, one obtains

$$\begin{aligned} \Gamma_j(\vec{q}, \omega, T) = & \frac{18\pi}{\hbar^2} \sum_{\substack{\vec{q}_1 \vec{q}_2 \\ j_1 j_2}} |V(j_1 \vec{q}_1 - j_2 \vec{q}_2)|^2 \Delta(\vec{q} - \vec{q}_1 - \vec{q}_2) \\ & \times \{(\bar{n}_1 + \bar{n}_2 + 1)[\delta(\omega_1 + \omega_2 - \omega) - \delta(\omega_1 + \omega_2 + \omega)] \\ & + (\bar{n}_2 - \bar{n}_1)[\delta(\omega_1 - \omega_2 - \omega) - \delta(\omega_1 - \omega_2 + \omega)]\} \quad . \end{aligned} \quad (5.153)$$

Here, $\bar{n}_i = \bar{n}(\vec{q}_i j_i)$ is the mean occupation number of the phonon $(\vec{q}_i j_i)$ with frequency $\omega_i = \omega_{j_i}(\vec{q}_i)$. ω is the applied frequency. The factor $\Delta(\vec{q} - \vec{q}_1 - \vec{q}_2)$ implies that the sum in this expression is to be taken over all modes $(\vec{q}_1 j_1)$ and $(\vec{q}_2 j_2)$ such that

$$\vec{q} - \vec{q}_1 - \vec{q}_2 = \vec{\tau} \quad . \quad (5.154)$$

Note that at $T = 0$, the damping is different from zero due to the zero-point energy and that at high temperatures, $\Gamma_j(\vec{q}, \omega, T)$ is proportional to T .

The real part of the self-energy has three contributions:

$$\Delta_j(\vec{q}, \omega) = \Delta_j^{(0)}(\vec{q}) + \Delta_j^{(1)}(\vec{q}) + \Delta_j^{(2)}(\vec{q}, \omega) \quad . \quad (5.155)$$

It will be noted that two of these are in fact independent of the applied frequency ω . The first, $\Delta_j^{(0)}(\vec{q})$, takes into account thermal expansion and for cubic crystals it can be written in the form

$$\Delta_j^{(0)}(\vec{q}) = -\gamma_j(\vec{q})\omega_j(\vec{q}) \frac{\Delta V}{V} \quad . \quad (5.156)$$

This term can be calculated using the quasiharmonic approximation, see (5.72,92). More general expressions are given in [5.28]. This term would be absent if the crystal were constrained to have a constant volume.

$\Delta_j^{(1)}(\vec{q})$ and $\Delta_j^{(2)}(\vec{q}, \omega)$ are due to the interactions of the phonon $(\vec{q} j)$ with the other phonons. $\Delta_j^{(1)}(\vec{q})$ originates from H_4 and is given by

$$\Delta_j^{(1)}(\vec{q}) = \frac{12}{\hbar} \sum_{\vec{q}_1 j_1} \nu \begin{pmatrix} \vec{q} & -\vec{q} & \vec{q}_1 & -\vec{q}_1 \\ j & j & j_1 & j_1 \end{pmatrix} (2\bar{n}_1 + 1) . \quad (5.157)$$

The last term in (5.155) is due to H_3 and has the form

$$\begin{aligned} \Delta_j^{(2)}(\vec{q}, \omega) = & \frac{18}{\hbar^2} \sum_{\substack{\vec{q}_1 \vec{q}_2 \\ j_1 j_2}} |\nu \begin{pmatrix} \vec{q} & -\vec{q}_1 & -\vec{q}_2 \\ j & j_1 & j_2 \end{pmatrix}|^2 \Delta(\vec{q} - \vec{q}_1 - \vec{q}_2) \times \\ & \times \left\{ (\bar{n}_1 + \bar{n}_2 + 1) \left[P\left(\frac{1}{\omega - \omega_1 - \omega_2}\right) - P\left(\frac{1}{\omega + \omega_1 + \omega_2}\right) \right] \right. \\ & \left. \times (\bar{n}_1 - \bar{n}_2) \left[P\left(\frac{1}{\omega + \omega_1 - \omega_2}\right) - P\left(\frac{1}{\omega - \omega_1 + \omega_2}\right) \right] \right\} . \end{aligned} \quad (5.158)$$

The actual calculations of $\Gamma_j(\vec{q}, \omega)$ and $\Delta_j^{(2)}(\vec{q}, \omega)$ are complicated by the presence of the delta functions in (5.153) and the principal parts in (5.158). These functions can be approximated by

$$\delta(x) = \frac{1}{\pi} \frac{\epsilon}{x^2 + \epsilon^2} , \quad P\left(\frac{1}{x}\right) = \frac{x}{x^2 + \epsilon^2} ,$$

where ϵ is a small and suitably chosen parameter [5.49]. Figure 5.13 shows calculations of $\Delta_j^{(2)}(0, \omega)$ and $\Gamma_j(0, \omega)$ for the T0-mode of KBr with frequency $\omega_j(0)$ as a function of both the applied frequency ω and the temperature [Ref. 4.11, p. 119]. Note that the damping and the shifts are quite small near $\omega_j(0)$. However, at other frequencies these quantities can be quite large. According to (5.153), the damping will be large at frequencies $\omega = \omega_1 \pm \omega_2$ due to the delta functions, especially if the joint density of states at these frequencies is large. The same is true for $\Delta_j^{(2)}(0, \omega)$ due to the principal parts. The marked structures in $\Gamma_j(0, \omega)$ and $\Delta_j^{(2)}(0, \omega)$, as shown in Fig. 5.13 for the case of KBr will lead to significant effects in the response function (5.141) and in the dielectric constant $\epsilon(\omega)$ given by (5.136). Such effects are, in fact, responsible for the subsidiary maxima observed in the infrared absorption bands [1.35].

The frequency dependence of the damping and shift of the T0-mode at $\vec{q} = 0$ has also been calculated for NaCl [5.50]. A breathing shell model was used to provide frequencies and eigenvectors necessary for these calculations. The influence of anharmonicity on the T0 and L0 optical phonons at $\vec{q} = 0$ has been studied experimentally by means of the far-infrared dielectric response for 18 alkali and thallium halides [5.51], for the silver and thallium halides

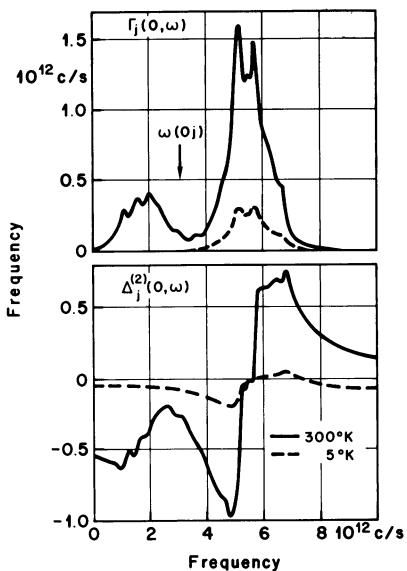


Fig. 5.13. Damping function $\Gamma_j(0, \omega)$ and $\Delta_j^{(2)}(0, \omega)$ calculated for the T0-mode at $\vec{q} = 0$ for KBr at $T = 300$ K and $T = 5$ K [5.49] and [Ref. 4.11, p. 119]

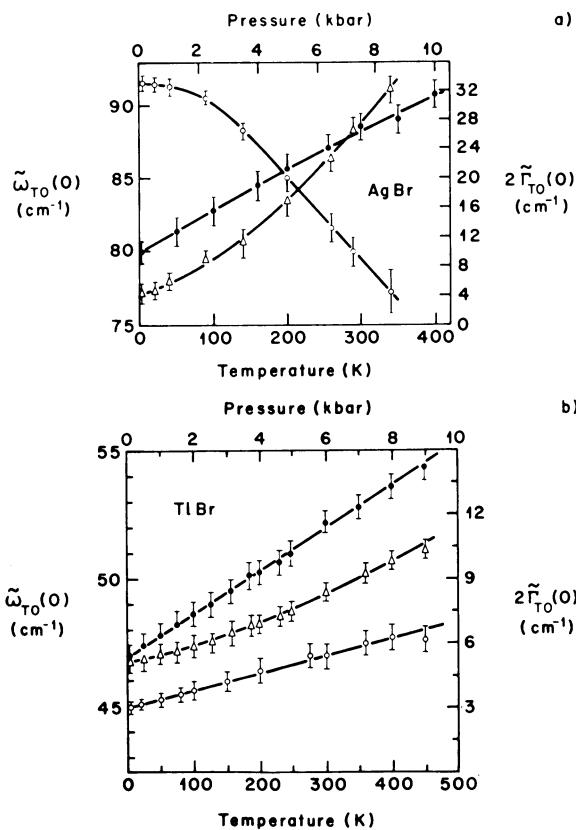


Fig. 5.14. The isobaric (10^{-5} bar) temperature dependence of the T0-mode at $\vec{q} = 0$ (open circle), its damping (open triangle) and the isothermal (290 K) pressure dependence of the T0-mode at $\vec{q} = 0$ (closed circle) for AgBr (a) and TlBr (b) [5.52]

[5.52] and for the alkaline earth fluorides [5.53]. Figure 5.14a shows the observed temperature and pressure dependence of the T0-mode frequency at $\vec{q} = 0$, $\tilde{\omega}_{T0}(0)$, and the temperature dependence of its damping, $2\tilde{\Gamma}_{T0}(0)$, for AgBr. Figure 5.14b gives the same information for TlBr; note that for TlBr, the frequency of the T0-mode *increases* with increasing temperature.

The different temperature dependence of the observed frequencies in different materials is due to the fact that the three contributions to $\Delta_j(\vec{q}, \tilde{\omega})$ of (5.155) are generally of the same order of magnitude but may have different signs; $\Delta_j(\vec{q}, \omega_j)$ may, therefore, be negative (which is generally the case) or positive. $\Delta_j^{(0)}(\vec{q})$ is normally negative; however, the sum $\Delta_j^{(1)}(\vec{q}) + \Delta_j^{(2)}(\vec{q}, \tilde{\omega}_j)$ may be negative (as for AgBr) or positive (as for TlBr) [5.52]. The magnitudes and signs of the individual contributions depend on the nature of the interatomic forces and cannot usually be predicted without detailed calculations based on (5.157,158), which involve the third and fourth or coupling parameters (Appendix P and [5.54]).

5.6 Problems

5.6.1 Thermal Expansion and Force Constant of Diatomic Molecules

Assuming the form (5.3) for the potential energy $\varphi(w_0)$, calculate the average displacement $\langle w_0 \rangle$ and the average force constant $\langle f \rangle$ by using the Boltzmann distribution function which weights the possible values of w_0 and $f = \partial^2 \varphi / \partial w_0^2$ according to their thermodynamic probabilities:

$$\langle w_0 \rangle = \frac{\int_{-\infty}^{+\infty} w_0 e^{-\beta \varphi(w_0)} dw_0}{\int_{-\infty}^{+\infty} e^{-\beta \varphi(w_0)} dw_0} ,$$

$$\langle f \rangle = \frac{\int_{-\infty}^{+\infty} (\partial^2 \varphi / \partial w_0^2) e^{-\beta \varphi(w_0)} dw_0}{\int_{-\infty}^{+\infty} e^{-\beta \varphi(w_0)} dw_0} .$$

Result:

$$\langle w_0(T) \rangle = -\frac{1}{2} \frac{g_0}{f_0^2} k_B T ,$$

$$\langle f(T) \rangle = f_0 - \frac{1}{2} \frac{g_0^2}{f_0^2} k_B T + \frac{3}{8} \frac{h_0}{f_0} k_B T .$$

5.6.2 Quantum Anharmonic Oscillator

Consider an anharmonic oscillator described by the Hamilton operator $H = H_0 + H'$, where

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 u^2$$

and

$$H' = a_3 u^3 + a_4 u^4 .$$

According to perturbation theory, the anharmonic contribution to the energy level E_n is given by

$$\Delta E_n = \langle n | H' | n \rangle - \sum_{n' \neq n} \frac{\langle n | H' | n' \rangle \langle n' | H' | n \rangle}{E_{n'}^{(0)} - E_n^{(0)}} ,$$

where $E_{n'}^{(0)}$ and $E_n^{(0)}$ are eigenvalues of H_0 . Show that the eigenvalues of H are given by

$$E_n = (n + \frac{1}{2})\hbar\omega + A(n^2 + n) + A_0 ,$$

where

$$A = \left(\frac{3}{4} a_4 - \frac{15}{4} \frac{a_3^2}{m\omega^2} \right) \left(\frac{\hbar}{m\omega} \right)^2$$

and

$$A_0 = \left(\frac{3}{4} a_4 - \frac{11}{8} \frac{a_3^2}{m\omega^2} \right) \left(\frac{\hbar}{m\omega} \right)^2 .$$

A_0 is the contribution of anharmonicity to the zero-point energy.

Hint: Express H' in terms of creation and annihilation operators a^+ and a , respectively, using the relation

$$u = \left(\frac{\hbar}{2m\omega} \right)^{\frac{1}{2}} (a^+ + a)$$

and apply the results analogously to (2.122,123), namely,

$$a^+ |n\rangle = (n + 1)^{\frac{1}{2}} |n + 1\rangle ,$$

$$a |n\rangle = n^{\frac{1}{2}} |n - 1\rangle ,$$

together with the orthogonality relations $\langle n | n' \rangle = \delta_{nn'}$. From this it follows that $\langle n | u^3 | n \rangle = 0$ but $\langle n | u^4 | n \rangle \neq 0$. The second-order term involving $a_4 u^4$ is of higher order than the first-order term $a_4 \langle n | u^4 | n \rangle$ and can be neglected, whereas the second-order term from $a_3 u^3$ is of the same order as $a_4 \langle n | u^4 | n \rangle$. In evaluating the matrix elements $\langle n | u^3 | n' \rangle$, only terms with $n' = n \pm 1$ and $n' = n \pm 3$ appear. One obtains

$$a_4 \langle n | u^4 | n \rangle = \frac{3}{2} a_4 \left(\frac{\hbar}{m\omega} \right)^2 (n^2 + n + \frac{1}{2})$$

$$\sum_{n' \neq n} \frac{\langle n | a_3 u^3 | n' \rangle \langle n' | a_3 u^3 | n \rangle}{E_{n'}^{(0)} - E_n^{(0)}} = \frac{15}{4} \frac{a^2}{\hbar\omega} \left(\frac{\hbar}{m\omega} \right)^3 (n^2 + n + \frac{11}{30}) .$$

5.6.3 Grüneisen Parameter, Thermal Expansion and Frequency Shift of a Monoatomic fcc Crystal

Consider an fcc crystal with one atom in the primitive unit cell and with an interatomic potential $\varphi(r)$ which extends only to nearest neighbours. Neglecting the tangential force constant, i.e., $\varphi'(r_0) = 0$, there is then only one radial force constant $\varphi''(r_0)$, where r_0 is the distance between nearest neighbours. This corresponds to a model where the atoms are held together by springs of force constant $\varphi''(r_0)$. In the notation of (3.141,142), we have $F = G = \varphi''(r_0)/2$, $H = 0$ and the eigenfrequencies can be written in the form

$$\omega_j(\vec{q}) = \left[\frac{2\varphi''(r_0)}{m} \right]^{\frac{1}{2}} \lambda_j(\vec{q}) ,$$

where $\lambda_j(\vec{q})$ is a dimensionless quantity which is independent of $\varphi''(r_0)$ and m . For example, when q is parallel to the (100) direction, it follows from (3.143) that

$$\lambda_1(\vec{q}) = \lambda_2(q) = \sqrt{2} \sin \frac{qa}{4}$$

for the transverse modes and

$$\lambda_3(\vec{q}) = 2 \sin \frac{qa}{4}$$

for the longitudinal modes.

- a) From the definition (5.72), calculate the Grüneisen parameter $\gamma_s = \gamma_j(\vec{q})$ by using the above expression for $\omega_j(\vec{q})$.

Result: $\gamma_s \equiv \gamma = -\frac{r_0}{6} \frac{\varphi'''(r_0)}{\varphi''(r_0)}$; independent of s.

b) From (5.85), calculate the thermal expansion $\epsilon = \Delta V/V_0$ at high temperatures, neglecting the zero-point energy.

Result: $\epsilon = \frac{\Delta V}{V_0} = 3 \frac{Nk_B T}{V_0} \kappa_0 \gamma$.

c) From (5.82), calculate the compressibility κ_0

Result: $\kappa_0 = \frac{3}{2\sqrt{2}} \frac{r_0}{\varphi''(r_0)}$.

d) From (5.156) and the results obtained in (a), (b) and (c), calculate the frequency shift $\Delta_j^{(0)}(\vec{q})$ due to thermal expansion.

Result: $\Delta_j^{(0)}(\vec{q}) = -\frac{1}{8} \frac{[\varphi'''(r_0)]^2}{[\varphi''(r_0)]^3} k_B T \omega_j(\vec{q})$.

5.6.4 Grüneisen Parameter of T0 and L0-Modes of Simple Diatomic Crystals

According to (5.72), the Grüneisen parameter of the mode s is given by

$$\gamma_s = -\frac{v_a}{\omega_s} \frac{\partial \omega_s}{\partial v_a},$$

where v_a is the volume of the primitive unit cell. For crystals with NaCl structure, $v_a = 2r_0^3$, where r_0 is the nearest-neighbour distance. Show that for this case,

$$\gamma_s = -\frac{1}{6} \frac{r_0^2}{\omega_s^2} \frac{\partial \omega_s^2}{\partial r_0}. \quad (1)$$

Using (4.56,62,65,66,72), show that in terms of the volume independent parameters b and ρ of the Born-Mayer potential (4.19), the T0 and L0-mode frequencies for $\vec{q} = 0$ of the NaCl structure are given by

$$\mu\omega_{T0}^2 = R_0 - \frac{2\pi}{3} \frac{(ze)^2}{r_0^3}; \quad \mu\omega_{L0}^2 = R_0 + \frac{4\pi}{3} \frac{(ze)^2}{r_0^3}, \quad (2)$$

where

$$R_0 = \frac{2b\sigma(\sigma - 2)}{r_0^2} e^{-\sigma} = \frac{\sigma - 2}{3} \alpha_M \frac{(ze)^2}{r_0^3} \quad (3)$$

and $\sigma = r_0/\rho$.

From (1, 2, 3), show that the Grüneisen parameters of the T0 and L0-modes are given by

$$\gamma_{T0} = \frac{(R_0/6)(\sigma^2 - 2\sigma - 2)/(\sigma - 2) - (\pi/3)(ze)^2/r_0^3}{R_0 - (2\pi/3)(ze)^2/r_0^3}$$

$$\gamma_{L0} = \frac{(R_0/6)(\sigma^2 - 2\sigma - 2)/(\sigma - 2) + (2\pi/3)(ze)^2/r_0^3}{R_0 + (4\pi/3)(ze)^2/r_0^3} .$$

For LiF, we have $r_0 = 2.010 \text{ \AA}$, $\rho = 0.244 \text{ \AA}$, $\sigma = 8.24$, $\alpha_M = 1.747558$ and $\alpha_M(ze)^2/r_0^3 = 0.4960 \text{ mdyn/\AA}$. From this, we obtain $\gamma_{T0} = 2.434$ and $\gamma_{L0} = 0.880$. We see that γ_{T0} is approximately three times γ_{L0} indicating a stronger temperature dependence of the $\vec{q} = 0$ T0-modes as compared to the L0-mode. This is also the case in other compounds and is born out by experimental results [5.55]. Similar calculations have been performed for polarizable ions [5.55].

5.6.5 Displacement-Displacement Correlation Function $\sigma_{\alpha\beta}(\ell\ell')$

In Appendix 0 we have obtained an expression for $\sigma_{\alpha\beta}(\ell\ell')$ from a variational principle, see (0.21). Prove this relation by expressing the displacement components $u_{\ell\alpha}$ in terms of creation and annihilation operators using (3.74), namely,

$$u_{\ell\alpha} = \left(\frac{\hbar}{2Nm}\right)^{\frac{1}{2}} \sum_{\vec{q}j} e_{\alpha}(\vec{q}) j \omega_j^{-\frac{1}{2}}(\vec{q}) e^{i\vec{q}\vec{r}} A_j(\vec{q}) ,$$

where $A_j(\vec{q}) = a_j^+(-\vec{q}) + a_j(\vec{q})$.

[Here, we do not distinguish between unrenormalized and normalized frequencies and eigenvectors, that is, we put $\hat{\omega}_j(\vec{q}) = \omega_j(\vec{q})$ and $\hat{e}_{\alpha}(\vec{q}) = e_{\alpha}(\vec{q})$].

Hint: Note that for a Bravais lattice, the eigenvectors $\vec{e}(\vec{j})$ are real. In evaluating the averages $\langle u_{\ell\alpha} u_{\ell'\beta} \rangle$, etc., it is necessary to calculate the averages $\langle A_j(\vec{q}) A_{j'}(\vec{q}') \rangle$. For this purpose, use the results of Sect.2.2.3 and in particular, $\langle a_s^+ a_s \rangle = \bar{n}_s$, $\langle a_s^- a_s^+ \rangle = 1 + \bar{n}_s$, where $s = (\vec{q}j)$. This gives

$$\begin{aligned} \langle A_j(\vec{q}) A_{j'}(\vec{q}') \rangle &= 2\Delta(\vec{q} + \vec{q}') \delta_{jj'} \frac{\bar{E}_j(\vec{q})}{\hbar\omega_j(\vec{q})} \\ &= \Delta(\vec{q} + \vec{q}') \delta_{jj'} \coth \frac{\hbar\omega_j(\vec{q})}{2k_B T} . \end{aligned}$$

For $\langle u_{\ell\alpha} u_{\ell'\beta} \rangle$, we obtain

$$\langle u_{\ell\alpha} u_{\ell'\beta} \rangle = \frac{\hbar}{2Nm} \sum_{\vec{q}, j} \frac{e_\alpha(\vec{q}) e_{\beta}(\vec{q})}{\omega_j(\vec{q})} e^{i\vec{q}\cdot\vec{r}_{\ell\ell'}} \coth \frac{\hbar\omega_j(\vec{q})}{2k_B T} .$$

5.6.6 Equations of Motion Including Damping and External Driving Forces

In the limit $\vec{q} \rightarrow 0$, we write for the equations of motion

$$\begin{aligned} m_\kappa \ddot{u}_\alpha(\kappa) \\ = - \sum_{\kappa' \beta} f_{\alpha\beta}(\kappa\kappa') u_\beta(\kappa') - 2m_\kappa \gamma_\alpha(\kappa) \dot{u}_\alpha(\kappa) + e_\kappa E_\alpha . \end{aligned}$$

The first term is the harmonic force with

$$f_{\alpha\beta}(\kappa\kappa') = \sum_{\ell} \Phi_{\alpha\beta}(\kappa\kappa') ;$$

the second term represents an ad hoc damping force which describes dissipation of energy; and the last term is the driving force acting on the charge e_κ due to the external field $E_\alpha = E_0 \exp(-i\omega t)$. Internal field effects are neglected and the ions are assumed to be rigid. Transforming to normal coordinates Q_j defined by

$$u_\alpha(\kappa) = m_\kappa^{-\frac{1}{2}} \sum_j e_\alpha(\kappa j) Q_j$$

and using the relations (3.22, 27, 29), show that in terms of Q_j , the equations of motion are

$$\ddot{Q}_j + \omega_j^2 Q_j + 2 \sum_{j'} \Gamma_{jj'} \dot{Q}_{j'} = k_j ,$$

where

$$k_j = \sum_{\kappa\alpha} m_\kappa^{-\frac{1}{2}} e_\kappa e_\alpha^*(\kappa j) E_\alpha$$

and

$$\Gamma_{jj'} = \sum_{\kappa\alpha} \gamma_\alpha(\kappa) e_\alpha^*(\kappa j) e_\alpha(\kappa j') .$$

In the following, we assume that the electric field is parallel to the direction α ($E_{\alpha'} = 0$ for $\alpha' \neq \alpha$), which leads to normal coordinates $Q_{j\alpha}$. Furthermore, we assume that $\Gamma_{jj'} = \delta_{jj'} \Gamma_j$ and obtain

$$\ddot{Q}_{j\alpha} + \omega_j^2 Q_{j\alpha} + 2\Gamma_j \dot{Q}_{j\alpha} = f_{j\alpha}^{\frac{1}{2}} E_\alpha ,$$

where

$$f_{j\alpha}^{\frac{1}{2}} = \sum_{\kappa} m_{\kappa}^{-\frac{1}{2}} e_{\kappa} e_{\alpha}^{*}(\kappa j) .$$

Using the Ansatz for a forced oscillation with frequency ω , namely, $Q_j = A_j \exp(-i\omega t)$, one obtains

$$Q_{j\alpha} = f_{j\alpha}^{\frac{1}{2}} R_j(0, \omega) E_{\alpha} ,$$

where the response function is given by

$$R_j(0, \omega) = (\omega_j^2 - \omega^2 - 2i\tau_j \omega)^{-1} .$$

From the dielectric constant $\epsilon_{\alpha} = 1 + 4\pi P_{\alpha}/E_{\alpha}$ and the polarization

$$P_{\alpha} = \frac{1}{4\pi} (\epsilon_{\infty\alpha} - 1) E_{\alpha} + \frac{1}{v_a} \sum_{\kappa} e_{\kappa} u_{\alpha}(\kappa) ,$$

show that

$$\epsilon_{\alpha}(\omega) = \epsilon_{\infty\alpha} + \sum_j S_{j\alpha} R_j(0, \omega) ,$$

where $S_{j\alpha} = (4\pi/v_a) f_{j\alpha}$ is the oscillator strength of mode j if the field is in the direction α . In the rigid-ion approximation considered above, $\epsilon_{\infty} = 1$. Calculate $S_{j\alpha}$ for the TO-mode at $\vec{q} = 0$ of alkali-halide crystals in the rigid-ion approximation using the appropriate eigenvectors which are similar to those defined by (2.41,42). Result: $S = 4\pi e^2/v_a u$.

Appendix

A) Periodicity of Eigenfrequencies and Atomic Displacements in Reciprocal Space

We prove (2.32a and b). From (2.12) we obtain

$$D(q + \tau) = B^+(\tau)D(q)B(\tau) , \quad (A.1)$$

where

$$B(\tau) = \begin{pmatrix} e^{i\tau x_1} & 0 \\ 0 & e^{i\tau x_2} \end{pmatrix} \quad (A.2)$$

and $\tau = 2\pi m/a$, $m = 0, \pm 1, \pm 2, \dots$

Since $D(q + \tau)$ and $D(q)$ are related by a similarity transformation, they have the same eigenvalues [2.5], thus

$$\Lambda(q + \tau) = \Lambda(q) . \quad (A.3a)$$

$$\text{or } \omega_j(q + \tau) = \omega_j(q) . \quad (A.3b)$$

From (2.17), we have

$$D(q)e(q) = e(q)\Lambda(q) . \quad (A.4)$$

Replacing q in this equation by $q + \tau$ and using (A.1 and 3a) and $B^+ = B^{-1}$, we obtain

$$D(q)B(\tau)e(q + \tau) = B(\tau)e(q + \tau)\Lambda(q) . \quad (A.5)$$

Comparison of (A.4) with (A.5) gives (within an arbitrary factor of modulus unity which we choose to be 1)

$$e(q + \tau) = B^+(\tau)e(q) \quad (A.6a)$$

or

$$e(\kappa|_j^{q+\tau}) = e^{-i\tau x_k} e(\kappa|_j^q) . \quad (A.6b)$$

The displacement of the atom (κ^{ℓ}) in the mode (j^q) is given by

$$u(\kappa^{\ell}|j^q) = \frac{1}{2} (N m_{\kappa})^{-\frac{1}{2}} \left(A(j^q) e(\kappa|j^q) \exp\{i[qx(\kappa^{\ell}) - \omega_j(q)t]\} + c.c. \right) . \quad (A.7)$$

Replacing q in this expression by $q + \tau$ and using (A.3b and 6b) and the same initial conditions for the modes (j^q) and $(j^{q+\tau})$ we obtain

$$u(\kappa^{\ell}|j^{q+\tau}) = u(\kappa^{\ell}|j^q) . \quad (A.8)$$

B) An Important Lattice Sum

We calculate the sum (2.51)

$$S_N(q'') = \sum_{\ell=1}^N e^{iq''\ell a} , \quad (B.1)$$

where $q'' = q - q'$.

a) If $q'' = \frac{2\pi}{a} p$ ($p = 0, \pm 1, \pm 2, \dots$) we obtain

$$S_N(q'' = \frac{2\pi}{a} p) = N . \quad (B.2)$$

b) If $q'' \neq \frac{2\pi}{a} p$, the summation of the geometric series gives

$$S_N(q'') = e^{iq''a} \frac{1 - e^{iq''Na}}{1 - e^{iq''a}} . \quad (B.3)$$

Applying periodic boundary conditions, we have, according to (2.34),

$$e^{iq''Na} = 1$$

and therefore

$$S_N(q'' \neq \frac{2\pi}{a} p) = 0 . \quad (B.4)$$

Summarizing these results we can write

$$\sum_{\ell=1}^N e^{i(q-q')\ell a} = N \Delta(q - q') \quad (B.5)$$

where

$$\Delta(q - q') = 1 \text{ for } q - q' = \frac{2\pi}{a} p$$

$$\Delta(q - q') = 0 \text{ for } q - q' \neq \frac{2\pi}{a} p . \quad (B.6)$$

C) Hamiltonian for the Diatomic Chain in Terms of Normal Coordinates

From (2.47) the momentum $p(\kappa) = m\dot{u}(\kappa)$ is given by

$$p(\kappa) = \left(\frac{m}{N}\right)^{\frac{1}{2}} \sum_{qj} e(\kappa|j^q) \exp[iqx(\kappa)] \dot{Q}(j^q) . \quad (C.1)$$

Substituting this expression in the kinetic energy in (2.3) gives

$$T = \frac{1}{2N} \sum_{\substack{qj \\ q'j'}} \dot{Q}(j^q) \dot{Q}(j'^{q'}) \sum_{\kappa} e(\kappa|j^q) e(\kappa|j'^{q'}) e^{i(q+q')x_{\kappa}} \sum_{\ell} e^{i(q+q')\ell a} .$$

According to (B.5), the sum over ℓ is different from zero only if $q' = -q$ (here q and q' are restricted to the first Brillouin zone). This result together with (2.48,31,25) leads to the expression

$$2T = \sum_{qj} \dot{Q}(j^q) \dot{Q}^*(j^q) . \quad (C.2)$$

The transformation of the potential energy in (2.3) is more complicated.

Substitution of (2.47) in the sums

$$S = \sum_{\ell} [u(\ell_2) - u(\ell_1)]^2 \quad \text{and} \quad S' = \sum_{\ell} [u(\ell_1 + 1) - u(\ell_2)]^2$$

and using (B.5) and (2.31,48) gives

$$\begin{aligned} S = & \sum_{qjj'} Q(j^q) Q^*(j^q) \left\{ m_1^{-1} e(1|j^q) e^*(1|j^q) + m_2^{-1} e(2|j^q) e^*(2|j^q) \right. \\ & \left. - (m_1 m_2)^{-\frac{1}{2}} [e(1|j^q) e^*(2|j^q) \varphi_{12} + e^*(1|j^q) e(2|j^q) \varphi_{12}^*] \right\} \end{aligned} \quad (C.3)$$

$$\begin{aligned} S' = & \sum_{qjj'} Q(j^q) Q^*(j^q) \left\{ m_1^{-1} e(1|j^q) e^*(1|j^q) + m_2^{-1} e(2|j^q) e^*(2|j^q) \right. \\ & \left. - (m_1 m_2)^{-\frac{1}{2}} [e(1|j^q) e^*(2|j^q) \psi_{12} + e^*(1|j^q) e(2|j^q) \psi_{12}^*] \right\} \end{aligned} \quad (C.4)$$

where $\varphi_{12} = \exp[iq(x_1 - x_2)]$ and $\psi_{12} = \exp[iq(x_1 - x_2 + a)]$. Substituting (C.3) and (C.4) in the potential energy and making use of the definitions (2.12) one obtains

$$\begin{aligned} \Phi = & \frac{1}{2} \sum_{qjj'} Q(j^q) Q^*(j^q) \left\{ [D_{11} e(1|j^q) + D_{12} e(2|j^q)] e^*(1|j^q) \right. \\ & \left. + [D_{21} e(1|j^q) + D_{22} e(2|j^q)] e^*(2|j^q) \right\} . \end{aligned} \quad (C.5)$$

Using (2.16 and 25) we finally obtain from (C.5)

$$\Phi = \frac{1}{2} \sum_{qj} \omega_j^2(q) Q_j(q) Q_j^*(q) . \quad (C.6)$$

D) Commutator Relations for Normal Coordinates

As we have discussed in Sect.2.2.1, the classical Hamilton function of an oscillator with mass m , eigenfrequency ω , displacement coordinate u and momentum p is given by

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 u^2 \quad (D.1)$$

and the transition to quantum mechanics is achieved by replacing the momentum p according to the rule

$$p = -i\hbar \frac{\partial}{\partial u} \quad (D.2)$$

by an operator. u and p satisfy the commutator relations

$$[u, p] = up - pu = i\hbar \quad (D.3a)$$

$$[u, u] = [p, p] = 0 . \quad (D.3b)$$

The relation (D.3a) means that both sides are to be applied on an arbitrary wave function ψ and thereby using the explicit expression (D.2) for p :

$$-i\hbar u \frac{\partial \psi}{\partial u} + i\hbar \frac{\partial}{\partial u} (u\psi) = i\hbar \psi . \quad (D.4)$$

Equation (D.4) is verified at once by differentiation of $u\psi$ according to the product rule. The relations (D.3b) are satisfied trivially. Since ψ is an arbitrary (differentiable) function, we can consider the relations (D.3) as identities. We have thus shown that the representation (D.2) is equivalent to the commutator relations (D.3).

For two particles $(\ell)_K$ and $(\ell')_K$ of our chain (ℓ, ℓ' number the unit cells, K , K' number the atoms in these unit cells), the generalization of (D.3) is

$$[u(\ell)_K, p(\ell')_K] = i\hbar \delta_{\ell\ell'} \delta_{KK'} \quad (D.5a)$$

$$[u(\ell)_K, u(\ell')_K] = [p(\ell)_K, p(\ell')_K] = 0 \quad (D.5b)$$

and in the u -representation this is equivalent to

$$p(\ell)_K = -i\hbar \frac{\partial}{\partial u(\ell)_K} . \quad (D.6)$$

Now, we first prove the commutator relations (2.112). From (2.53 and 56) we obtain

$$\begin{aligned} C_1 &= [Q^*(\frac{q}{j}), P(\frac{q'}{j'})] \\ &= N^{-1} \sum_{\ell \in \kappa} \sum_{\ell' \in \kappa'} e(\kappa | \frac{q}{j}) e^*(\kappa' | \frac{q'}{j'}) \exp[iqx(\frac{\ell}{\kappa}) - iq'x(\frac{\ell'}{\kappa'})] [u(\frac{\ell}{\kappa}), p(\frac{\ell'}{\kappa'})] . \end{aligned}$$

Using (D.5a), we obtain

$$C_1 = i\hbar N^{-1} \sum_{\kappa} e(\kappa | \frac{q}{j}) e^*(\kappa | \frac{q'}{j'}) e^{i(q-q')x(\kappa)} \sum_{\ell} e^{i(q-q')\ell a} ,$$

and applying (B.5) and (2.25) we find

$$C_1 = [Q^*(\frac{q}{j}), P(\frac{q'}{j'})] = i\hbar \Delta(q - q') \delta_{jj'} . \quad (D.7a)$$

In the same way we obtain

$$[Q(\frac{q}{j}), P^*(\frac{q'}{j'})] = i\hbar \Delta(q - q') \delta_{jj'} . \quad (D.7b)$$

If we use in addition (2.31), we find in a similar way

$$C_2 = [Q(\frac{q}{j}), P(\frac{q'}{j'})] = [Q^*(\frac{q}{j}), P^*(\frac{q'}{j'})] = i\hbar \Delta(q + q') \delta_{jj'} . \quad (D.8)$$

From (D.5b) it is seen without any calculation that all commutators involving only Q' or only P 's are all zero, for example,

$$[Q^*(\frac{q}{j}), Q(\frac{q'}{j'})] = [P^*(\frac{q}{j}), P(\frac{q'}{j'})] = 0 . \quad (D.9)$$

Based on (2.67 and 68) we now calculate the commutator $[\eta(\frac{q}{j}), \zeta(\frac{q}{j})]$. Using the condensed notation $s = (qj)$ and $s' = (q'j')$ we find with the help of (D.9)

$$\begin{aligned} [\eta_s, \zeta_{s'}] &= \frac{1}{4} ([Q_s^*, P_{s'}] + [Q_s, P_{s'}^*] - [Q_s, P_{s'}] - [Q_s^*, P_{s'}^*]) \\ &\quad + \frac{\omega_{s'}}{4\omega_s} ([Q_{s'}^*, P_s] + [Q_{s'}, P_s^*] + [Q_{s'}, P_s] + [Q_{s'}^*, P_s^*]) . \end{aligned}$$

Due to (D.8) and $\omega_j(-q) = \omega_j(q)$, the commutators of the form $[Q_s, P_{s'}]$ and $[Q_s^*, P_{s'}^*]$ cancel and with (D.7) we obtain

$$[\eta(\frac{q}{j}), \zeta(\frac{q'}{j'})] = i\hbar \Delta(q - q') \delta_{jj'} . \quad (D.10a)$$

Similarly, we find

$$[\eta(\frac{q}{j}), \eta(\frac{q'}{j'})] = [\zeta(\frac{q}{j}), \zeta(\frac{q'}{j'})] = 0 . \quad (D.10b)$$

We have seen before that in the u -representation the commutator relations (D.5) are equivalent to (D.6). Now we can conclude that in the n -representation, the commutator relations (D.10) are equivalent to

$$\zeta_j^q = -i\hbar \frac{\partial}{\partial n_j^q} . \quad (\text{D.11})$$

Hence, we have shown that (D.11) follows from (D.6).

E) The Occupation Number Representation

We shall first derive (2.122 and 123). From (2.121), we obtain

$$a_s^+ a_s^+ |n_{s_1} \dots n_s \dots\rangle = (n_s + 1) a_s^+ |n_{s_1} \dots n_s \dots\rangle . \quad (\text{E.1})$$

This equation shows that the function $a_s^+ |n_{s_1} \dots n_s \dots\rangle$ is an eigenfunction of the operator $a_s^+ a_s$ which belongs to the eigenvalue $n_s + 1$ and as such must be proportional to $|n_{s_1} \dots n_s + 1 \dots\rangle$. We write therefore

$$a_s^+ |n_{s_1} \dots n_s \dots\rangle = N^+(n_s) |n_{s_1} \dots n_s + 1 \dots\rangle , \quad (\text{E.2})$$

where $N^+(n_s)$ is a normalizing factor which is still to be determined.

We now calculate $a_s^+ a_s^+ a_s |n_{s_1} \dots n_s \dots\rangle$. From (2.117) it follows that

$$[a_s^+ a_s, a_s] = a_s^+ a_s a_s - a_s a_s^+ a_s = [a_s^+, a_s] a_s = -a_s$$

and we obtain $a_s^+ a_s^+ a_s = a_s (a_s^+ a_s - 1)$. Applying the right hand side of this equation to $|n_{s_1} \dots n_s \dots\rangle$, we obtain with (2.120)

$$a_s^+ a_s^+ a_s |n_{s_1} \dots n_s \dots\rangle = (n_s - 1) a_s |n_{s_1} \dots n_s \dots\rangle . \quad (\text{E.3})$$

Thus, $a_s |n_{s_1} \dots n_s \dots\rangle$ is an eigenfunction of $a_s^+ a_s$ belonging to the eigenvalue $n_s - 1$ and therefore we can write

$$a_s |n_{s_1} \dots n_s \dots\rangle = N^-(n_s) |n_{s_1} \dots n_s - 1 \dots\rangle . \quad (\text{E.4})$$

The normalization factors $N^+(n_s)$ and $N^-(n_s)$ are determined from the orthogonality condition (2.107)

$$\langle n_{s_1} \dots n_s \dots | n_{s_1} \dots n_s \dots \rangle = 1 \quad (\text{E.5})$$

and from the matrix elements of $a_s^+ a_s$ and $a_s a_s^+$. First we note that from (2.120, 121), and (E.5), it follows that

$$\langle n_{s_1} \dots n_s \dots | a_s^+ a_s | n_{s_1} \dots n_s \dots \rangle = n_s \quad (E.6)$$

$$\langle n_{s_1} \dots n_s \dots | a_s a_s^+ | n_{s_1} \dots n_s \dots \rangle = n_s + 1 \quad . \quad (E.7)$$

On the other hand we obtain from (E.4), (E.2), and (E.5)

$$\begin{aligned} & \langle n_{s_1} \dots n_s \dots | a_s^+ a_s | n_{s_1} \dots n_s \dots \rangle \\ &= N^-(n_s) \langle n_{s_1} \dots n_s \dots | a_s^+ | n_{s_1} \dots n_s - 1 \dots \rangle \\ &= N^-(n_s) N^+(n_s - 1) \langle n_{s_1} \dots n_s \dots | n_{s_1} \dots n_s \dots \rangle \\ &= N^-(n_s) N^+(n_s - 1) \end{aligned} \quad (E.8)$$

and similarly,

$$\langle n_{s_1} \dots n_s \dots | a_s a_s^+ | n_{s_1} \dots n_s \dots \rangle = N^+(n_s) N^-(n_s + 1) \quad . \quad (E.9)$$

Comparing (E.6) with (E.8) and (E.7) with (E.9), we obtain

$$\begin{aligned} N^-(n_s) N^+(n_s - 1) &= n_s \\ N^+(n_s) N^-(n_s + 1) &= n_s + 1 \quad . \end{aligned} \quad (E.10)$$

Equations (E.10) are satisfied for $N^+(n_s) = (n_s + 1)^{\frac{1}{2}}$ and $N^-(n_s) = n_s^{\frac{1}{2}}$. From (E.2) and (E.4) we therefore obtain the important relations

$$a_s^+ | n_{s_1} \dots n_s \dots \rangle = (n_s + 1)^{\frac{1}{2}} | n_{s_1} \dots n_s + 1 \dots \rangle \quad (E.11)$$

$$a_s | n_{s_1} \dots n_s \dots \rangle = n_s^{\frac{1}{2}} | n_{s_1} \dots n_s - 1 \dots \rangle \quad . \quad (E.12)$$

From these equations, we immediately obtain the individual matrix elements

$$\langle n'_s | a_s^+ | n_s \rangle = (n_s + 1)^{\frac{1}{2}} \delta_{n'_s, n_s + 1} \quad (E.13)$$

$$\langle n'_s | a_s | n_s \rangle = n_s^{\frac{1}{2}} \delta_{n'_s, n_s - 1} \quad . \quad (E.14)$$

From (2.113, 114) and (E.11), (E.12) we can calculate the expectation values of $Q_j^{(q)}$ and $P_j^{(q)}$. Using the condensed notation $s = (qj)$ and $-s = (-qj)$, we obtain

$$\langle n_{s_1} \dots n_{-s} \dots n_s \dots | P_s | n_{s_1} \dots n_{-s} \dots n_s \dots \rangle =$$

$$\begin{aligned}
 &= i \left(\frac{\hbar \omega_s}{2} \right)^{\frac{1}{2}} \{ \langle n_{s_1} \dots n_{-s} \dots | a_{-s}^+ | n_{s_1} \dots n_{-s} \dots \rangle \\
 &\quad - \langle n_{s_1} \dots n_s \dots | a_s | n_{s_1} \dots n_s \dots \rangle \} \\
 &= i \left(\frac{\hbar \omega_s}{2} \right)^{\frac{1}{2}} (n_{-s} + 1)^{\frac{1}{2}} \langle n_{s_1} \dots n_{-s} \dots | n_{s_1} \dots n_{-s} + 1 \dots \rangle \\
 &\quad - i \left(\frac{\hbar \omega_s}{2} \right)^{\frac{1}{2}} n_s^{\frac{1}{2}} \langle n_{s_1} \dots n_s \dots | n_{s_1} \dots n_s - 1 \dots \rangle .
 \end{aligned}$$

However, due to the orthogonality of the wave functions (2.107), the above brackets are zero and we obtain the result

$$\langle n_{s_1} \dots n_s \dots | P_s | n_{s_1} \dots n_s \dots \rangle = 0 \quad (\text{E.15})$$

and a similar derivation gives

$$\langle n_{s_1} \dots n_s \dots | Q_s | n_{s_1} \dots n_s \dots \rangle = 0 . \quad (\text{E.16})$$

F) Restriction on Atomic Force Constants Which Follow from the Space Group Symmetry of the Crystal

The equilibrium configuration of a crystal [with all displacement vectors $\vec{u}_k^{(\ell)} = 0$] is transformed into itself by a number of symmetry elements g which form the *space group* of the crystal structure. If a crystal which is in a given distorted configuration [with $\vec{u}_k^{(\ell)} \neq 0$] is acted upon by a symmetry operation g , a new distorted configuration will result which may be different from the old one but which will always be equivalent to the old one in the sense that the same interatomic distances and angles occur in both configurations. Figure F.1 shows this situation for the case of the planar carbonate ion $(\text{CO}_3)^{-2}$, where the transformation of the displacement vectors by the vertical plane of symmetry σ_v is shown.

Since the potential energy Φ depends on the interatomic distances and angles, it will be identical in the two configurations and we can write

$$g\Phi = \Phi . \quad (\text{F.1})$$

This invariance condition yields the relations between the force constants. Before we establish these relations we consider the structure of the elements g . The most general symmetry operation which sends the crystal into itself is a combination of a rotation of the crystal about some point plus a translation of the crystal. We represent such a symmetry operation by

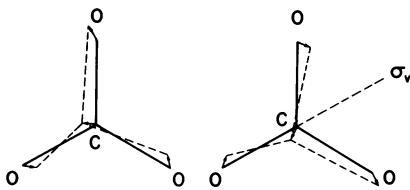


Fig.F.1. The effect of the vertical mirror plane σ_v to the displacement vectors of the atoms of the carbonate ion CO_3^{2-}

$$g = [S | \vec{v}(S) + \vec{t}(m)] . \quad (\text{F.2})$$

S is a 3×3 real, orthogonal matrix representation of one of the proper or improper rotations of the point group of the space group, $\vec{v}(S)$ is a vector associated with S which is smaller than any primitive translation vector and $\vec{t}(m) = \sum m_i \vec{a}_i$, where \vec{a}_i are the primitive translation vectors and $m_i = 0, \pm 1, \pm 2, \dots$. The vectors $\vec{v}(S)$ are associated with the symmetry elements called glide planes and screw axes. Space groups for which $\vec{v}(S)$ is identically zero for every rotation S of the point group of the space group are called *symmorphic*. Space groups with $\vec{v}(S) \neq 0$ are called *nonsymmorphic*.

According to (3.3) the actual position of the atom $(\ell)_K$ is given by

$$\vec{R}(\ell)_K = \vec{r}(\ell)_K + \vec{u}(\ell)_K , \quad (\text{F.3})$$

where $\vec{u}(\ell)_K$ is the displacement vector of the atom $(\ell)_K$ from its equilibrium position $\vec{r}(\ell)_K$. If g is applied to $\vec{R}(\ell)_K$, we obtain

$$g\vec{R}(\ell)_K = S\vec{r}(\ell)_K + \vec{v}(S) + \vec{t}(m) . \quad (\text{F.4})$$

Substituting (F.3) in (F.4) yields

$$\begin{aligned} g\vec{R}(\ell)_K &= S\vec{r}(\ell)_K + \vec{v}(S) + \vec{t}(m) + S\vec{u}(\ell)_K \\ &= g\vec{r}(\ell)_K + S\vec{u}(\ell)_K . \end{aligned}$$

Since g is an element which transforms the crystal into itself, the point $(\ell)_K$ is transformed into an equivalent point $(g\ell)_{gK}$ and we can write

$$g\vec{r}(\ell)_K = \vec{r}(g\ell)_{gK} \quad (\text{F.5})$$

and we obtain the result

$$\vec{gR}(\ell_k) = \vec{r}(g_k^\ell) + \vec{Su}(\ell_k) . \quad (F.6)$$

The potential energy is a function of the positions $\vec{R}(\ell_k)$:

$$\Phi = \Phi(\dots \vec{R}(\ell_k) \dots \vec{R}(\ell_{k'}) \dots) .$$

The invariance of Φ with respect to g can be expressed by

$$\begin{aligned} \Phi(\dots \vec{R}(\ell_k) \dots \vec{R}(\ell_{k'}) \dots) \\ = \Phi(\dots \vec{gR}(\ell_k) \dots \vec{gR}(\ell_{k'}) \dots) . \end{aligned} \quad (F.7)$$

Using (F.6), we obtain

$$\begin{aligned} \Phi(\dots \vec{r}(\ell_k) + \vec{u}(\ell_k), \dots \vec{r}(\ell_{k'}) + \vec{u}(\ell_{k'}), \dots) \\ = \Phi(\dots \vec{r}(g_k^\ell) + \vec{Su}(\ell_k), \dots \vec{r}(g_{k'}^\ell) + \vec{Su}(\ell_{k'}), \dots) . \end{aligned} \quad (F.8)$$

Equation (F.8) shows that Φ can be developed in a Taylor's series about the transformed equilibrium positions $\vec{r}(g_k^\ell)$ as well, but the variables are now the transformed displacements $\vec{Su}(\ell_k)$. Confining ourselves to the harmonic energy, we therefore obtain

$$\Phi = \frac{1}{2} \sum_{\substack{\ell \in \alpha, \\ \ell' \in \alpha'}} \Phi_{\alpha' \beta'} (g_k^\ell g_{k'}^{\ell'}) (\vec{Su}(\ell_k))_\alpha (\vec{Su}(\ell_{k'}))_{\beta'} .$$

With

$$\begin{aligned} [\vec{Su}(\ell_k)]_\alpha &= \sum_\alpha S_{\alpha' \alpha} u_\alpha(\ell_k) \\ [\vec{Su}(\ell_{k'})]_{\beta'} &= \sum_{\beta'} S_{\beta' \beta} u_{\beta'}(\ell_{k'}) , \end{aligned}$$

we obtain

$$\Phi = \frac{1}{2} \sum_{\substack{\ell \in \alpha, \\ \ell' \in \alpha'}} \left\{ \sum_{\alpha' \beta'} S_{\alpha' \alpha} S_{\beta' \beta} \Phi_{\alpha' \beta'} (g_k^\ell g_{k'}^{\ell'}) \right\} u_\alpha(\ell_k) u_{\beta'}(\ell_{k'}) . \quad (F.9)$$

On the other hand we have

$$\Phi = \frac{1}{2} \sum_{\substack{\ell \in \alpha, \\ \ell' \in \alpha'}} \Phi_{\alpha \beta} (\ell \ell') u_\alpha(\ell_k) u_{\beta'}(\ell_{k'}) . \quad (F.10)$$

Comparing the coefficients of (F.9) and (F.10) we obtain the relations

$$\Phi_{\alpha \beta} (\ell \ell') = \sum_{\alpha' \beta'} S_{\alpha' \alpha} S_{\beta' \beta} \Phi_{\alpha' \beta'} (g_k^\ell g_{k'}^{\ell'}) . \quad (F.11)$$

Let $\Phi_{\alpha\beta}^{(\ell\ell')}(KK')$ be a 3×3 matrix with elements $\Phi_{\alpha\beta}^{(\ell\ell')}(KK')$. Equation (F.11) can then be written in the form

$$\Phi_{\alpha\beta}^{(\ell\ell')}(KK') = S^T \Phi_{\alpha\beta}^{(g\ell\ g\ell')}(g_K\ g_{K'}) S . \quad (\text{F.12a})$$

Since $S^{-1} = S^T$ we obtain

$$\Phi_{\alpha\beta}^{(g\ell\ g\ell')}(g_K\ g_{K'}) = S \Phi_{\alpha\beta}^{(\ell\ell')}(KK') S^T \quad (\text{F.12b})$$

or

$$\Phi_{\alpha\beta}^{(g\ell\ g\ell')}(g_K\ g_{K'}) = \sum_{\alpha'\beta'} S_{\alpha\alpha'} S_{\beta\beta'} \Phi_{\alpha'\beta'}^{(\ell\ell')}(KK') . \quad (\text{F.12c})$$

An important special case is obtained when we specialize the space group element $\{S|\vec{v}(S) + \vec{t}(m)\}$ to the operation $\{E|\vec{t}(m)\}$, where E is the 3×3 unit matrix; this is the operation of displacing the crystal through the lattice translation $\vec{t}(m)$. In this case $g\ell = \ell + m$, $g_K = K$ and (F.12b) yields

$$\Phi_{\alpha\beta}^{(\ell+m\ \ell'+m)}(K\ K') = \Phi_{\alpha\beta}^{(\ell\ell')}(KK') . \quad (\text{F.13})$$

As an application, we consider the force constants in the simple cubic lattice shown in Fig.(F.2). The atom at (000) has 6 nearest neighbours at a distance d , 12 second nearest neighbours at a distance $\sqrt{2}d$ and 8 third nearest neighbours at a distance $\sqrt{3}d$. According to (3.17b)

$$\Phi_{\alpha\beta}^{(\ell\ell')}(KK') = - \sum_{\substack{\ell' \\ (K') \neq (\ell)}} \Phi_{\alpha\beta}^{(\ell\ell')}(KK') \quad (\text{F.14})$$

and it is, therefore, only necessary to consider the elements $\Phi_{\alpha\beta}^{(\ell\ell')}(KK')$ with $(K') \neq (\ell)$. For these elements we use the notation

$$\Phi_{\alpha\beta}^{(\ell\ell')}(KK') = \Phi_{\alpha\beta}^{(\vec{L})} , \quad \vec{L} = \vec{r}(\ell') - \vec{r}(\ell) ,$$

and (F.12b) can be rewritten in the form

$$\Phi(g\vec{L}) = S \Phi(\vec{L}) S^T . \quad (\text{F.15})$$

For the 6 nearest neighbour atoms, the vectors \vec{L} are

$$\vec{L}_{1.2} = \pm d(1,0,0), \quad \vec{L}_{3.4} = \pm d(0,1,0), \quad \vec{L}_{5.6} = \pm d(0,0,1) .$$

If we consider a space group element of the form $g = \{S|0\}$ where S is a rotation about the x -axis or a reflection through the xz -plane (Fig.F.2), then $g\vec{L}_1 = \vec{L}_1$. For $S = C_{2x}$ = rotation by an angle 180° about the x -axis we have

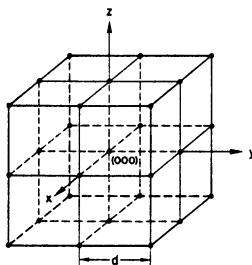


Fig.F.2. Neighbours of the central atom at (0,0,0) in the simple cubic lattice

$$C_{2x} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

and dropping the symbol \vec{L}_1 the relation (F.15) gives $\phi_{xy} = \phi_{yx} = \phi_{xz} = \phi_{zx} = 0$. Similarly, the application of the mirror plane

$$\sigma_{xz} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

gives $\phi_{yz} = \phi_{zy}$. Finally the rotation

$$C_{4x} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$$

by the angle 90° about the x-axis results in $\phi_{yy} = \phi_{zz}$. The matrix $\phi(\vec{L}_1)$ is therefore diagonal and has the form

$$\phi(\vec{L}_1) = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix} \quad (F.16a)$$

If $S = I$ = center of symmetry we have

$$I = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

and we obtain $g\vec{L} = -\vec{L}$ and $\phi(-\vec{L}) = I\phi(\vec{L})I$ which yields

$$\phi(\vec{L}_1) = \phi(-\vec{L}_1) = \phi(\vec{L}_2), \quad \phi(\vec{L}_3) = \phi(\vec{L}_4),$$

$$\phi(\vec{L}_5) = \phi(\vec{L}_6).$$

For $\phi(\vec{L}_3)$ and $\phi(\vec{L}_5)$, we obtain by an analogous procedure

Table F.1: Force constants of the simple cubic lattice shown in Fig.F.2

\vec{L}	$\pm d(1,0,0)$	$\pm d(0,1,0)$	$\pm d(0,0,1)$
$\Phi(\vec{L})$	$\begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix}$	$\begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$	$\begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix}$
\vec{L}	$\pm d(1,1,0)$	$\pm d(1,0,1)$	$\pm d(0,1,1)$
$\Phi(\vec{L})$	$\begin{pmatrix} \beta' & \gamma' & 0 \\ \gamma' & \beta' & 0 \\ 0 & 0 & \alpha' \end{pmatrix}$	$\begin{pmatrix} \beta' & 0 & \gamma' \\ 0 & \alpha' & 0 \\ \gamma' & 0 & \beta' \end{pmatrix}$	$\begin{pmatrix} \alpha' & 0 & 0 \\ 0 & \beta' & \gamma' \\ 0 & \gamma' & \beta' \end{pmatrix}$
\vec{L}	$\pm d(1,1,1)$	$\pm d(-1,1,1)$	$\pm d(1,-1,1)$
$\Phi(\vec{L})$	$\begin{pmatrix} \alpha'' & \gamma'' & \gamma'' \\ \gamma'' & \alpha'' & \gamma'' \\ \gamma'' & \gamma'' & \alpha'' \end{pmatrix}$	$\begin{pmatrix} \alpha'' & -\gamma'' & -\gamma'' \\ -\gamma'' & \alpha'' & \gamma'' \\ -\gamma'' & \gamma'' & \alpha'' \end{pmatrix}$	$\begin{pmatrix} \alpha'' & -\gamma'' & \gamma'' \\ -\gamma'' & \alpha'' & -\gamma'' \\ \gamma'' & -\gamma'' & \alpha'' \end{pmatrix}$
\vec{L}	$\pm d(1,1,1)$	$\pm d(-1,1,1)$	$\pm d(1,-1,1)$
$\Phi(\vec{L})$	$\begin{pmatrix} \alpha' & \gamma' & \gamma' \\ \gamma' & \alpha' & \gamma' \\ \gamma' & \gamma' & \alpha' \end{pmatrix}$	$\begin{pmatrix} \beta' & -\gamma' & 0 \\ -\gamma' & \beta' & 0 \\ 0 & 0 & \alpha' \end{pmatrix}$	$\begin{pmatrix} \beta' & 0 & -\gamma' \\ 0 & \alpha' & 0 \\ -\gamma' & 0 & \beta' \end{pmatrix}$
\vec{L}	$\pm d(1,1,1)$	$\pm d(-1,1,1)$	$\pm d(1,-1,1)$
$\Phi(\vec{L})$	$\begin{pmatrix} \alpha'' & \gamma'' & \gamma'' \\ \gamma'' & \alpha'' & \gamma'' \\ \gamma'' & \gamma'' & \alpha'' \end{pmatrix}$	$\begin{pmatrix} \alpha'' & -\gamma'' & \gamma'' \\ -\gamma'' & \alpha'' & -\gamma'' \\ \gamma'' & -\gamma'' & \alpha'' \end{pmatrix}$	$\begin{pmatrix} \alpha'' & \gamma'' & -\gamma'' \\ \gamma'' & \alpha'' & -\gamma'' \\ -\gamma'' & -\gamma'' & \alpha'' \end{pmatrix}$

$$\phi(\vec{L}_3) = \phi(\vec{L}_4) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}, \quad (\text{F.16b})$$

$$\phi(\vec{L}_5) = \phi(\vec{L}_6) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix}. \quad (\text{F.16c})$$

By similar considerations, we also obtain the force constant matrices for second and third neighbours. These results are summarized in Table F.1 [3.18].

G) Dynamical Matrix

We prove that the dynamical matrix $D(\vec{q})$ is Hermitian:

$$D_{\beta\alpha}(\vec{q}_{kk'}) = D_{\alpha\beta}^*(\vec{q}_{kk'}) .$$

From (3.23), we obtain

$$D_{\beta\alpha}(\vec{q}_{kk'}) = \frac{e^{i\vec{q}[\vec{r}(k)-\vec{r}(k')]} }{(m_k m_{k'})^{\frac{1}{2}}} \sum_{L'} \phi_{\beta\alpha}(0, L') e^{i\vec{q}\vec{r}(L')} .$$

Using (3.16) and $\vec{r}(-L') = -\vec{r}(L')$ from 3.1 gives

$$\begin{aligned} D_{\beta\alpha}(\vec{q}_{kk'}) &= \frac{e^{-i\vec{q}[\vec{r}(k')-\vec{r}(k)]}}{(m_k m_{k'})^{\frac{1}{2}}} \sum_{L'} \phi_{\alpha\beta}(L' 0) e^{-i\vec{q}\vec{r}(-L')} \\ &= \frac{e^{-i\vec{q}[\vec{r}(k')-\vec{r}(k)]}}{(m_k m_{k'})^{\frac{1}{2}}} \sum_{L'} \phi_{\alpha\beta}(0 -L') e^{-i\vec{q}\vec{r}(-L')} , \end{aligned}$$

where in the latter equation we have used (3.19). Since $L' = 0, \pm 1, \pm 2$, we can replace $-L'$ by L' in the sum and obtain

$$D_{\beta\alpha}(\vec{q}_{kk'}) = \frac{e^{-i\vec{q}[\vec{r}(k')-\vec{r}(k)]}}{(m_k m_{k'})^{\frac{1}{2}}} \sum_{L'} \phi_{\alpha\beta}(0 L') e^{-i\vec{q}\vec{r}(L')} = D_{\alpha\beta}^*(\vec{q}_{kk'}) .$$

H) Acoustic Modes for $\vec{q} \rightarrow 0$

For $\vec{q} = 0$, we obtain from (3.22,27)

$$\sum_{\ell' k' \beta} \frac{\phi_{\alpha\beta}(\ell\ell')}{m_k} \frac{e_{\beta}(k'|j)}{m_{k'}^{\frac{1}{2}}} = \omega_j^2(0) \frac{e_{\alpha}(k|j)}{m_k^{\frac{1}{2}}} . \quad (\text{H.1})$$

From this equation, it follows that the components $e_{\beta}(\kappa' | j)^0$ are real and from (3.20) we obtain

$$u_{\beta}(\kappa' | j)^0 = \frac{1}{2} N^{-\frac{1}{2}} \frac{e_{\beta}(\kappa' | j)^0}{m_{\kappa'}^{\frac{1}{2}}} [A(0)e^{-i\omega_j(0)t} + c.c.] ,$$

where $u_{\beta}(\kappa' | j)^0$ is the displacement of atom (κ') in the β -direction for the mode (j) . Hence, we obtain

$$\frac{e_{\beta}(\kappa' | j)^0}{m_{\kappa'}^{\frac{1}{2}}} = k u_{\beta}(\kappa' | j)^0 , \quad (H.2)$$

where k is a coefficient independent of ℓ' and κ' . If the mode $(j)^0$ represents a translation of the whole crystal in the β -direction by a distance v_{β} , we can put $u_{\beta}(\kappa' | j)^0 = v_{\beta}$ and the quantity

$$\frac{e_{\beta}(\kappa' | j)^0}{m_{\kappa'}^{\frac{1}{2}}} = k v_{\beta} \quad (H.3)$$

is independent of ℓ' and κ' . Substituting (H.3) in (H.1), we obtain

$$m_{\kappa}^{-1} \sum_{\beta} v_{\beta} \sum_{\ell' \kappa'} \Phi_{\alpha\beta}(\ell' \ell') = \omega_j^2(0) v_{\alpha} . \quad (H.4)$$

Now, from (3.17a) we have that

$$\sum_{\ell' \kappa'} \Phi_{\alpha\beta}(\ell' \ell') = 0 ,$$

and if we exclude the trivial solution $v_x = v_y = v_z = 0$, (H.4) shows that there are three solutions, one for each value of α , which vanish with vanishing \vec{q} . Such modes are called acoustic modes.

I) The Hamilton Function in Terms of \dot{Q} and $P = \dot{Q}$

The transformation of the kinetic energy

$$T = \frac{1}{2} \sum_{\ell \kappa \alpha} m_{\kappa} \dot{u}_{\alpha}^2(\ell) \quad (I.1)$$

is performed exactly as in Appendix C. Substituting (3.53) in (I.1) and using (3.66, 31, 29, 54) one obtains

$$T = \frac{1}{2} \sum_{\vec{q} j} \dot{Q}(\vec{q}) \dot{Q}^*(\vec{q}) = \frac{1}{2} \sum_{\vec{q} j} P(\vec{q}) P^*(\vec{q}) . \quad (I.2)$$

Substituting (3.53) in the potential energy (3.13)

$$\Phi = \frac{1}{2} \sum_{\substack{\ell \kappa \alpha \\ \ell' \kappa' \beta}} \Phi_{\alpha \beta}(\ell \ell') u_\alpha(\ell \kappa) u_\beta(\ell' \kappa') , \quad (I.3)$$

we obtain

$$2\Phi = \frac{1}{N} \sum_{\substack{\vec{q}_j \\ \vec{q}'_j}} Q(\vec{q}_j) Q(\vec{q}'_j) \sum_{\substack{\kappa \alpha \\ \kappa' \beta}} e_\alpha(\kappa | \vec{q}_j) e_\beta(\kappa' | \vec{q}'_j) \\ \times \sum_{\ell \ell'} \frac{\Phi_{\alpha \beta}(\ell \ell')}{(m_\kappa m_{\kappa'})^{\frac{1}{2}}} \exp\{i[\vec{q} \cdot \vec{r}(\ell \kappa) + \vec{q}' \cdot \vec{r}(\ell' \kappa')]\} .$$

Multiplying this equation by $\exp\{i\vec{q}' \cdot [\vec{r}(\ell \kappa) - \vec{r}(\ell' \kappa')]\} = 1$ and making use of the definition (3.22) for the dynamical matrix and the relation (3.66), we obtain

$$2\Phi = \sum_{\substack{\vec{q}_{jj'} \\ \vec{q}_{jj'}}} Q(\vec{q}_j) Q(-\vec{q}_{j'}) \sum_{\kappa \alpha} e_\alpha(\kappa | \vec{q}_j) \sum_{\kappa' \beta} D_{\alpha \beta}(-\vec{q}_{j'}) e_\beta(\kappa' | -\vec{q}_{j'}) .$$

From (3.27, 31, 54) and $D(-\vec{q}) = D^*(\vec{q})$ we obtain

$$2\Phi = \sum_{\substack{\vec{q}_{jj'} \\ \vec{q}_{jj'}}} Q(\vec{q}_j) Q^*(\vec{q}_{j'}) \omega_j^2(\vec{q}) \sum_{\kappa \alpha} e_\alpha^*(\kappa | \vec{q}_{j'}) e_\alpha(\kappa | \vec{q}_j) .$$

Application of (3.29) gives the result

$$\Phi = \frac{1}{2} \sum_{\vec{q}_j} \omega_j^2(\vec{q}) Q(\vec{q}) Q^*(\vec{q}) . \quad (I.4)$$

J) Force Constants for Central Forces

The potential energy of the crystal is

$$\Phi = \frac{1}{2} \sum_{ik} \varphi(R_{ik}) , \quad (J.1)$$

where the index i stands for the atom (ℓ) and k for the atom (ℓ') . From Fig.J.1 we have $\vec{R}_{ik} = \vec{r}_{ik} + \vec{u}_{ik}$, $\vec{r}_{ik} = \vec{r}_k - \vec{r}_i$, and $\vec{u}_{ik} = \vec{u}_k - \vec{u}_i$. Let $R_{ik\alpha}$, $r_{ik\alpha}$, and $u_{ik\alpha}$ be the components of \vec{R}_{ik} , \vec{r}_{ik} , and \vec{u}_{ik} , respectively. Developing $\varphi(R_{ik})$ in a Taylor series we obtain

$$\varphi(R_{ik}) = \varphi(r_{ik}) + \sum_{\alpha} \varphi_{\alpha}(ik) u_{ik\alpha} + \frac{1}{2} \sum_{\alpha \beta} \varphi_{\alpha \beta}(ik) u_{ik\alpha} u_{ik\beta} + \dots \quad (J.2)$$

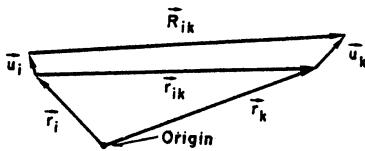


Fig.J.1. \vec{r}_i and \vec{r}_k are the vectors defining the equilibrium positions of the atoms i and k , respectively. \vec{u}_i and \vec{u}_k are the corresponding displacement vectors

where the prime at the summation sign indicates that $i \neq k$, and

$$\varphi_{\alpha}(ik) = \left(\frac{\partial \varphi}{\partial R_{ik\alpha}} \right)_0 = \left(\frac{\partial \varphi}{\partial u_{ik\alpha}} \right)_0 \quad (J.3)$$

$$\varphi_{\alpha\beta}(ik) = \left(\frac{\partial^2 \varphi}{\partial R_{ik\alpha} \partial R_{ik\beta}} \right)_0 = \left(\frac{\partial^2 \varphi}{\partial u_{ik\alpha} \partial u_{ik\beta}} \right)_0 \quad . \quad (J.4)$$

Substituting (J.2) in (J.1) and using $u_{ik\alpha} = u_{k\alpha} - u_{i\alpha}$, etc., the harmonic term of Φ becomes

$$\Phi_h = \frac{1}{2} \sum'_{i\alpha} \varphi_{\alpha\beta}(ik) (u_{i\alpha} u_{i\beta} - u_{i\alpha} u_{k\beta}) \quad . \quad (J.5)$$

This expression must be compared with (3.13), namely

$$\Phi_h = \frac{1}{2} \sum'_{i\alpha} \varphi_{\alpha\beta}(ik) u_{i\alpha} u_{k\beta} \quad . \quad (J.6)$$

From (J.5) and (J.6) it follows immediately that

$$\varphi_{\alpha\beta}(ik) = -\varphi_{\alpha\beta}(ik) \quad \text{for } i \neq k \quad (J.7)$$

and

$$\varphi_{\alpha\beta}(ii) = \sum'_{k\beta} \varphi_{\alpha\beta}(ik) \quad . \quad (J.8)$$

For central forces the derivatives $\varphi_{\alpha\beta}(ik)$ can be calculated easily. Introducing

$$\varphi' = \frac{\partial \varphi}{\partial R} \text{ and } \varphi'' = \frac{\partial^2 \varphi}{\partial R^2} \quad , \quad (J.9)$$

one obtains

$$\frac{\partial \varphi}{\partial R_\alpha} = \frac{R_\alpha}{R} \varphi'$$

$$\frac{\partial^2 \varphi}{\partial R_\alpha \partial R_\beta} = \frac{1}{R} \left(\delta_{\alpha\beta} - \frac{R_\alpha R_\beta}{R^2} \right) \varphi' + \frac{R_\alpha R_\beta}{R^2} \varphi'' \quad ,$$

and $\varphi_{\alpha\beta}(ik)$ is given by

$$\varphi_{\alpha\beta}(ik) = \frac{r_{ik\alpha} r_{ik\beta}}{r_{ik}^2} [\varphi''(r_{ik}) - r_{ik}^{-1}\varphi'(r_{ik})] + \delta_{\alpha\beta} r_{ik}^{-1}\varphi'(r_{ik}) . \quad (\text{J.10})$$

From (J.10) and (J.7) we obtain

$$\Phi_{\alpha\beta}(ik) = -F(r_{ik})r_{ik\alpha}r_{ik\beta} - \delta_{\alpha\beta}G(r_{ik}) , \quad (\text{J.11})$$

where

$$F(r_{ik}) = \frac{1}{r_{ik}^2} [\varphi''(r_{ik}) - r_{ik}^{-1}\varphi'(r_{ik})] , \quad (\text{J.12})$$

$$G(r_{ik}) = r_{ik}^{-1}\varphi'(r_{ik}) . \quad (\text{J.13})$$

K) Evaluation of the Coulomb Matrix Using Ewald's Method

The Coulomb matrix $C(\vec{q})$ is defined by (4.32). If we explicitly separate out the term $\Phi_{\alpha\beta}^{(C)}(\ell\ell')_{KK}$ in this equation and use (3.17b), we obtain

$$\begin{aligned} & z_{\kappa} z_{\kappa'} C_{\alpha\beta}(\vec{q},) \\ &= \sum'_{\ell'} \Phi_{\alpha\beta}^{(C)}(\ell\ell')_{KK'} \exp\{i\vec{q}[\vec{r}_{\kappa'}^{\ell'}] - \vec{r}_{\kappa}^{\ell'}]\} - \delta_{KK'} \sum''_{\kappa''} \sum'_{\ell'} \Phi_{\alpha\beta}^{(C)}(\ell\ell'')_{KK''} . \end{aligned} \quad (\text{K.1})$$

In the first sum the term with $\ell' = \ell$ is to be excluded if $\kappa' = \kappa$ and in the second one if $\kappa'' = \kappa$. Let $\varphi^{(C)}(R)_{KK}$ be the Coulomb energy between the ions κ and κ' separated by a distance R . By definition, the force constants are

$$\Phi_{\alpha\beta}^{(C)}(\ell\ell')_{KK'} = -\left(\frac{\partial^2 \varphi^{(C)}(R)}{\partial R_{\alpha} \partial R_{\beta}}\right)_{R=\vec{r}_{\kappa'}^{\ell'}-\vec{r}_{\kappa}^{\ell'}} . \quad (\text{K.2})$$

Defining quantities

$$N_{\alpha\beta}(\vec{q},) = -\sum'_{\ell'} \left[e^{i\vec{q}\vec{R}} \left(\frac{\partial^2 \varphi^{(C)}(R)}{\partial R_{\alpha} \partial R_{\beta}} \right) \right]_{R=\vec{r}_{\kappa'}^{\ell'}-\vec{r}_{\kappa}^{\ell'}} , \quad (\text{K.3})$$

(K.1) can be written in the form

$$z_{\kappa} z_{\kappa'} C_{\alpha\beta}(\vec{q},) = N_{\alpha\beta}(\vec{q},) - \delta_{KK'} \sum''_{\kappa''} N_{\alpha\beta}(0)_{KK''} . \quad (\text{K.4})$$

Following Ewald's method we write according to (4.34)

$$\varphi^{(C)}(R)_{KK'} = \varphi^{(G)}(R)_{KK'} + \varphi^{(H)}(R)_{KK'} . \quad (\text{K.5})$$

Substitution of (K.5) in (K.3) gives

$$N_{\alpha\beta}(\vec{q}_{kk'}) = N_{\alpha\beta}^{(G)}(\vec{q}_{kk'}) + N_{\alpha\beta}^{(H)}(\vec{q}_{kk'}) , \quad (K.6)$$

where

$$N_{\alpha\beta}^{(G)}(\vec{q}_{kk'}) = - \sum'_{\ell} \left(e^{iq\vec{R}} \frac{\partial^2 \varphi^{(G)}(R_{kk'})}{\partial R_\alpha \partial R_\beta} \right)_{\vec{R}=\vec{r}(k')-\vec{r}(k)} . \quad (K.7)$$

and

$$N_{\alpha\beta}^{(H)}(\vec{q}_{kk'}) = - \sum'_{\ell} \left(e^{iq\vec{R}} \frac{\partial^2 \varphi^{(H)}(R_{kk'})}{\partial R_\alpha \partial R_\beta} \right)_{\vec{R}=\vec{r}(k')-\vec{r}(k)} . \quad (K.8)$$

We now evaluate $\varphi^{(H)}(R_{kk'})$. From (K.5) and (4.20) it follows that

$$\varphi^{(H)}(R_{kk'}) = z_k z_{k'} \frac{e^2}{R} - \varphi^{(G)}(R_{kk'}) . \quad (K.9)$$

The second term in (K.9) is the potential energy of a point charge $z_k e$ at a point \vec{R} in a three-dimensional Gaussian charge distribution $\varphi_k^{(G)}$ defined by (4.33) (Fig.4.3). It is given by

$$\varphi^{(G)}(R_{kk'}) = z_k e \left[\frac{1}{R} \int_0^R \rho_{k'}^{(G)}(R') d^3 R' + \int_R^\infty \frac{\rho_{k'}^{(G)}(R')}{R'} d^3 R' \right] . \quad (K.10)$$

The first term is the contribution from $\rho_{k'}^{(G)}$ lying inside a sphere of radius R about the origin, and the second is from that part lying outside the sphere. From the normalization condition

$$\int_0^\infty \rho_{k'}^{(G)}(R') d^3 R' = z_{k'} e ,$$

and (K.10) it follows that (K.9) can be rewritten in the form

$$\varphi^{(H)}(R_{kk'}) = z_k e \int_R^\infty \left(\frac{1}{R} - \frac{1}{R'} \right) \rho_{k'}^{(G)}(R') d^3 R' . \quad (K.11)$$

Using (4.33) and $d^3 R' = 4\pi R'^2$, one obtains

$$\varphi^{(H)}(R_{kk'}) = 2z_k z_{k'} e^2 \left(\frac{n}{\pi} \right)^{1/2} \frac{1}{R} \int_R^\infty e^{-nR'^2} dR' . \quad (K.12)$$

This quantity decreases rapidly with increasing R and therefore behaves like a short range potential, provided n is suitably chosen. The sum for $N_{\alpha\beta}^{(H)}(\vec{q}_{kk'})$ defined by (K.8) therefore converges rapidly. The situation is different for $N_{\alpha\beta}^{(G)}(\vec{q}_{kk'})$. From (K.10) we see that $\varphi^{(G)}(R_{kk'})$ has the characteristics of the Coulomb potential at large distances and hence the sum in (K.7) can not be evaluated directly. In order to obtain a rapid convergent series, we express

$N_{\alpha\beta}^{(G)}(\vec{q})$ in terms of the Fourier transform of $\varphi^{(G)}(R)$: Let \vec{Q} be a general vector in reciprocal space (not to be confused with the normal coordinates Q !). $\varphi^{(G)}(R)$ and its Fourier transform $\varphi^{(G)}(Q)$ are related by

$$\varphi^{(G)}(R) = \frac{1}{(2\pi)^3} \int \varphi^{(G)}(Q) e^{-i\vec{Q}\vec{R}} d^3Q . \quad (K.13)$$

Substituting (K.13) in (K.7) and differentiation with respect to R_α and R_β gives

$$N_{\alpha\beta}^{(G)}(\vec{q}) = \frac{1}{(2\pi)^3} \int d^3Q Q_\alpha Q_\beta \varphi^{(G)}(Q) \\ \times e^{-i(\vec{Q}-\vec{q})[\vec{r}(k')-\vec{r}(k)]} \sum_L e^{-i(\vec{Q}-\vec{q})\vec{r}(L)} ,$$

where $\vec{r}(L) = \vec{r}(l') - \vec{r}(l)$. Using the result

$$\sum_L e^{-i(\vec{Q}-\vec{q})\vec{r}(L)} = \frac{(2\pi)^3}{V_a} \sum_{\vec{\tau}} \delta(\vec{Q} - \vec{q} - \vec{\tau}) , \quad (K.14)$$

we obtain

$$N_{\alpha\beta}^{(G)}(\vec{q}) = \frac{1}{V_a} \sum_{\vec{\tau}} d^3Q Q_\alpha Q_\beta \varphi^{(G)}(Q) \\ \times e^{-i(\vec{Q}-\vec{q})[\vec{r}(k')-\vec{r}(k)]} \delta(\vec{Q} - \vec{q} - \vec{\tau}) .$$

Applying the condition

$$\int f(\vec{Q}) \delta(\vec{Q} - \vec{q} - \vec{\tau}) d^3Q = f(\vec{\tau} + \vec{q}) \quad (K.15)$$

results in the following relation

$$N_{\alpha\beta}^{(G)}(\vec{q}) = \frac{1}{V_a} \sum_{\vec{\tau}} (\vec{\tau} + \vec{q})_\alpha (\vec{\tau} + \vec{q})_\beta \\ \times \varphi^{(G)}(|\vec{\tau} + \vec{q}|) e^{-i\vec{\tau}[\vec{r}(k')-\vec{r}(k)]} . \quad (K.16)$$

This is the \vec{Q} -space formulation of $N^{(G)}(\vec{q})$. It applies for any potential $\varphi(R)$ which depends only on the distance R between the atoms. In order to find $\varphi^{(G)}(Q)$, we use Poisson's theorem

$$\nabla^2 \varphi^{(G)}(R) = -4\pi z_k e_p^{(G)}(R) . \quad (K.17)$$

Applying this equation to (K.13) gives

$$\int Q^2 \varphi^{(G)}(Q) \frac{d^3Q}{(2\pi)^3} = 4\pi z_k e_p^{(G)}(R)$$

which yields

$$\begin{aligned} Q^2 \varphi^{(G)}(\frac{Q}{\kappa\kappa'}) &= 4\pi z_{\kappa} e \int \rho_{\kappa'}^{(G)}(R) e^{i\vec{QR}} d^3 R \\ &= 4\pi z_{\kappa} z_{\kappa'} e^2 \left(\frac{\eta}{\pi}\right)^{3/2} \int e^{-\eta R^2} e^{i\vec{QR}} d^3 R = 4\pi z_{\kappa} z_{\kappa'} e^2 e^{-Q^2/4\eta} \end{aligned}$$

from which we find

$$\varphi^{(G)}(\frac{Q}{\kappa\kappa'}) = \frac{4\pi z_{\kappa} z_{\kappa'} e^2}{Q^2} e^{-Q^2/4\eta} . \quad (K.18)$$

Substituting (K.18) in (K.16) we obtain the final result

$$\begin{aligned} N_{\alpha\beta}^{(G)}(\frac{\vec{q}}{\kappa\kappa'}) &= 4\pi z_{\kappa} z_{\kappa'} \frac{e^2}{\sqrt{a}} \sum_{\vec{\tau}} \frac{(\vec{\tau} + \vec{q})_{\alpha} (\vec{\tau} + \vec{q})_{\beta}}{|\vec{\tau} + \vec{q}|^2} \\ &\times \exp(-|\vec{\tau} + \vec{q}|^2/4\eta) e^{i\vec{\tau}[\vec{r}(\kappa) - \vec{r}(\kappa')]} . \end{aligned} \quad (K.19)$$

L) The Valence Force Model

1) Internal Coordinates and Their Relation to Atomic displacements

The relation (4.129) is written in the form

$$r_t = \sum_{\kappa} \vec{f}_{t\kappa} \vec{u}_{\kappa} , \quad (L.1)$$

where $\vec{u}_{\kappa} = (u_{\kappa x}, u_{\kappa y}, u_{\kappa z})$ and $\vec{s}_{t\kappa} = (B_{t,\kappa x}, B_{t,\kappa y}, B_{t,\kappa z})$.

a) *Stretching Coordinates:* $r_t = \Delta r_{12}$

From Fig.L.1, it follows that $\vec{r}'_{12} = \vec{r}_{12} + (\vec{u}_2 - \vec{u}_1)$ and $r'_{12} = r_{12} + \Delta r_{12}$.

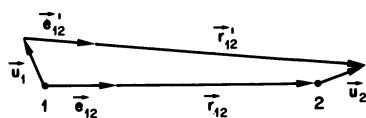


Fig.L.1. The figure illustrates the calculation of the stretching coordinate Δr_{12} in terms of the displacements \vec{u}_1 and \vec{u}_2

Thus we have

$$r_{12}'^2 \approx r_{12}^2 + 2\vec{r}_{12}(\vec{u}_2 - \vec{u}_1) \approx r_{12}^2 + 2r_{12}\Delta r_{12}$$

and

$$\Delta r_{12} \simeq \frac{\vec{r}_{12}}{r_{12}} (\vec{u}_2 - \vec{u}_1) = -\vec{e}_{12}\vec{u}_1 + \vec{e}_{12}\vec{u}_2 ,$$

and we obtain

$$\begin{aligned} \vec{f}_{t1} &= -\vec{e}_{12} & \vec{f}_{t2} &= +\vec{e}_{12} \\ \vec{r}_t &= \Delta r_{12} = \vec{e}_{12}(\vec{u}_2 - \vec{u}_1) . \end{aligned} \quad (L.2)$$

b) *Bending Coordinates:* $r_t = \sqrt{r_{31}r_{32}} \Delta\alpha$

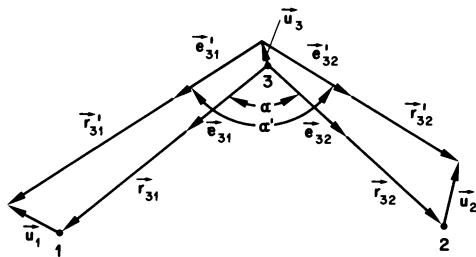


Fig.L.2. The figure illustrates the calculation of the bending coordinate $\Delta\alpha$ in terms of the displacements \vec{u}_1 , \vec{u}_2 , and \vec{u}_3

Using $\vec{e}_{3K'} = \vec{e}_{3K} + \Delta\vec{e}_{3K}$ we have $\Delta\cos\alpha = \cos(\alpha + \Delta\alpha) - \cos\alpha \approx -\Delta\alpha\sin\alpha$, or

$$\Delta\alpha = -\frac{\Delta\cos\alpha}{\sin\alpha} \approx -\frac{\vec{e}_{31}\Delta\vec{e}_{32} + \vec{e}_{32}\Delta\vec{e}_{31}}{\sin\alpha} . \quad (L.3)$$

From $\vec{e}_{3K} = \vec{r}_{3K}/r_{3K}$ we obtain

$$\Delta\vec{e}_{3K} = \frac{r_{3K}\Delta\vec{r}_{3K} - \Delta r_{3K}\vec{r}_{3K}}{r_{3K}^2} . \quad (L.4)$$

Substituting (L.4) in (L.3) and using $\Delta\vec{r}_{3K} = \vec{u}_K - \vec{u}_3$ and $\Delta r_{3K} = \vec{e}_{3K}(\vec{u}_K - \vec{u}_3)$, we obtain

$$\begin{aligned} \vec{f}_{t1} &= \sqrt{r_{31}r_{32}} \frac{\cos\alpha\vec{e}_{31} - \vec{e}_{32}}{r_{31}\sin\alpha} , \\ \vec{f}_{t2} &= \sqrt{r_{31}r_{32}} \frac{\cos\alpha\vec{e}_{32} - \vec{e}_{31}}{r_{32}\sin\alpha} , \\ \vec{f}_{t3} &= -(\vec{f}_{t1} + \vec{f}_{t2}) . \end{aligned} \quad (L.5)$$

Additional internal coordinates are discussed in [4.19].

2) Dynamical Matrix for the Valence Force Model

The potential energy is

$$2\Phi = \sum_{\ell\ell'} r^T(\ell') F_{\ell,\ell'} r(\ell) = N \sum_{\ell} r^T(0) F_{0,\ell} r(\ell) , \quad (L.6)$$

where N is the number of unit cells. Let $R(\vec{q})$ be translationally symmetrized coordinates defined by

$$R(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{\ell} r(\ell) e^{i\vec{q}\vec{r}(\ell)} , \quad (L.7)$$

from which it follows that

$$r(\ell) = \frac{1}{\sqrt{N}} \sum_{\vec{q}} R(\vec{q}) e^{-i\vec{q}\vec{r}(\ell)} \quad (L.8)$$

and

$$r^T(0) = \frac{1}{\sqrt{N}} \sum_{\vec{q}'} R^T(\vec{q}') , \quad (L.9)$$

where we have used $\vec{r}(0) = 0$ in (L.9). Substituting (L.8) and (L.9) in (L.6), we obtain

$$2\Phi = \sum_{\vec{q}\vec{q}'} R^T(\vec{q}') F(\vec{q}) R(\vec{q}) , \quad (L.10)$$

with

$$F(\vec{q}) = \sum_{\ell} F_{0,\ell} e^{-i\vec{q}\vec{r}(\ell)} . \quad (L.11)$$

We now use the fact that Φ is invariant against translations of the crystal lattice. If T_h is an operator describing a translation h we have $T_h r(\ell) = r(\ell + h)$ from which it follows from (L.7) that

$$R'(\vec{q}) = T_h R(\vec{q}) = e^{-i\vec{q}\vec{r}(h)} R(\vec{q}) \quad (L.12)$$

and we obtain

$$2\Phi' = \sum_{\vec{q}\vec{q}'} e^{-i(\vec{q}+\vec{q}')\vec{r}(h)} R^T(\vec{q}') F(\vec{q}) R(\vec{q}) = 2\Phi .$$

From this relation, it follows that $\vec{q}' = -\vec{q}$ and

$$2\Phi = \sum_{\vec{q}} R^T(\vec{q}) F(\vec{q}) R(\vec{q}) . \quad (L.13)$$

Using the transformation

$$r(\ell) = \sum_m B_{\ell,m} u(m) \quad (L.14)$$

and the fact that due to the periodicity of the crystal $B_{\ell,m} = B_{0,m-\ell}$, we obtain from (L.7)

$$R(\vec{q}) = B(\vec{q})U(\vec{q}) \quad , \quad (L.15)$$

where

$$U(\vec{q}) = \frac{1}{\sqrt{N}} \sum_m u(m) e^{i\vec{q}\vec{r}(m)}$$

and

$$B(\vec{q}) = \sum_{\ell} B_{0,\ell} e^{-i\vec{q}\vec{r}(\ell)} \quad . \quad (L.16)$$

Substituting (L.15) in (L.13) gives

$$2\Phi = \sum_{\vec{q}} U^{\dagger}(\vec{q}) M(\vec{q}) U(\vec{q}) \quad , \quad (L.17)$$

where

$$M(\vec{q}) = B^{\dagger}(\vec{q}) F(\vec{q}) B(\vec{q}) \quad . \quad (L.18)$$

M) The Saddle-Point Method

We want to calculate the integral appearing in (5.37),

$$I = \int_{-\infty}^{+\infty} F(s) ds = \int_{-\infty}^{+\infty} e^{Nz(s)} ds \quad . \quad (M.1)$$

The function $F(s)$ has a saddle point at $s = s_0$ defined by $z'(s_0) = 0$. It is shown below that s_0 is a point on the imaginary axis. Since $F(s)$ is an analytic function the integration path can be deformed in such a way as to pass through s_0 and $F(s_0)$ is a maximum for that path. Since N is large, this maximum is very sharp. The saddle-point method essentially consists of developing $F(s)$ around the saddle point; thus we write

$$z(s) \approx z(s_0) + \frac{1}{2} z''(s_0)(s - s_0)^2 \quad (M.2)$$

and obtain

$$I \approx e^{Nz(s_0)} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}N|z''(s_0)|(s-s_0)^2} ds \quad , \quad (M.3)$$

where we have used the fact that $z''(s_0) < 0$.

Using

$$\int_{-\infty}^{+\infty} e^{-\lambda x^2} dx = (\pi/\lambda)^{\frac{1}{2}},$$

we obtain

$$I \simeq \left(\frac{2\pi}{N|z''(s_0)|} \right)^{\frac{1}{2}} e^{Nz(s_0)} . \quad (M.4)$$

In order to determine s_0 we carry out the integrations in (5.38) and find

$$e^z(s)$$

$$\simeq \left(\frac{2\pi k_B T}{f} \right)^{\frac{1}{2}} (1 - 3\beta Hy^2 + \frac{15}{2} \beta^2 G^2 y^3 + 3i\beta Gy^2 s - \frac{1}{2} ys^2) , \quad (M.5)$$

where $y = k_B T/f$. From $z'(s_0) = 0$, we find

$$s_0 = 3i\beta G k_B T / f = (g/2f)i . \quad (M.6)$$

Substitution of (M.6) in (M.5) yields

$$e^z(s_0) \simeq \left(\frac{2\pi k_B T}{f} \right)^{\frac{1}{2}} (1 - 3\beta Hy^2 + 3\beta^2 G^2 y^3) . \quad (M.7)$$

From (5.37) and (M.1,4), we obtain

$$Z_\Phi = (2\pi N|z''(s_0)|)^{-\frac{1}{2}} e^{-\beta N\varphi(a)} e^{Nz(s_0)} , \quad (M.8)$$

and from (5.20) we find

$$F_\Phi = \frac{1}{2} k_B T \ln[2\pi N|z''(s_0)|] + N\varphi(a) - Nk_B T z(s_0) . \quad (M.9)$$

Using $\ln(1+x) \simeq x$ in (M.7) and neglecting the term of the order $\ln N$ in (M.9) yields

$$F_\Phi = N\varphi(a) - \frac{1}{2} Nk_B T \ln \left(\frac{2\pi k_B T}{f} \right) + N(k_B T)^2 \left(\frac{1}{8} \frac{h}{f^2} - \frac{1}{12} \frac{g^2}{f^3} \right) . \quad (M.10)$$

N) The Free Energy in the Harmonic or Quasiharmonic Approximation

The vibrational free energy of the crystal is defined by

$$F_{\text{vib}} = -k_B T \ln Z_{\text{vib}} , \quad (N.1)$$

where Z_{vib} is the vibrational partition function. The total vibrational energy of the crystal is given by

$$\begin{aligned} E_{\text{vib}}\{n_s\} &= E_{\text{vib}}(n_1, \dots, n_s, \dots, n_{3nN}) \\ &= \sum_{s=1}^{3nN} E_{n_s} = \sum_{s=1}^{3nN} (n_s + \frac{1}{2})\hbar\omega_s , \end{aligned} \quad (\text{N.2})$$

where $s = (\vec{q}, j)$ labels the phonons. Thus we have

$$Z_{\text{vib}} = \sum_{\{n_s\}} e^{-E_{\text{vib}}\{n_s\}/k_B T} = \prod_{s=1}^{3nN} Z_{\text{vib},s} , \quad (\text{N.3})$$

where

$$\begin{aligned} Z_{\text{vib},s} &= \sum_{n_s=0}^{\infty} e^{-\hbar\omega_s(n_s+\frac{1}{2})k_B T} \\ &= (e^{\hbar\omega_s/2k_B T} - e^{-\hbar\omega_s/2k_B T})^{-1} \end{aligned} \quad (\text{N.4})$$

is the partition function of phonon s . Substituting (N.3) in (N.1) yields

$$F_{\text{vib}} = -k_B T \sum_s \ln Z_{\text{vib},s} . \quad (\text{N.5})$$

Making use of (N.4) and of $\sinh(x) = [\exp(x) - \exp(-x)]/2$, we obtain

$$\begin{aligned} F_{\text{vib}} &= k_B T \sum_{s=1}^{3nN} \ln \left\{ 2 \sinh \frac{\hbar\omega_s}{2k_B T} \right\} \\ &= \frac{1}{2} \sum_s \hbar\omega_s + k_B T \sum_s \ln(1 - e^{-\hbar\omega_s/k_B T}) . \end{aligned} \quad (\text{N.6})$$

0) The Self-Consistent Harmonic Approximation (SCHA)

We consider a crystal of identical atoms which interact pairwise by a potential $\varphi(\vec{R})$. The latter is assumed to be a function of the magnitude of the pair separation only. For simplicity, we restrict ourselves to a Bravais lattice. The Hamiltonian of the system is

$$H = T_{\text{kin}} + \Phi , \quad (0.1)$$

where T_{kin} is the kinetic energy and the potential energy is given by

$$\Phi = \frac{1}{2} \sum'_{\ell\ell'} \varphi(\vec{R}_{\ell\ell'}) = \frac{1}{2} \sum'_{\ell\ell'} \varphi(\vec{r}_{\ell\ell'} + \vec{w}_{\ell\ell'}) . \quad (0.2)$$

Here, $\vec{r}_{\ell\ell'}$, are vectors joining the mean positions of the atoms and $\vec{w}_{\ell\ell'}$, $= \vec{u}_\ell - \vec{u}_{\ell'}$, are the relative displacement vectors. We now consider an effective harmonic Hamiltonian

$$\hat{H} = T_{\text{kin}} + \hat{\phi} \quad , \quad (0.3)$$

where

$$\hat{\phi} = \frac{1}{4} \sum'_{\ell\ell'} \hat{\varphi}_{\alpha\beta}(\ell\ell') w_{\ell\ell'\alpha} w_{\ell\ell'\beta} \quad . \quad (0.4)$$

Both the force constants $\hat{\varphi}_{\alpha\beta}(\ell\ell')$ and the mean distances $r_{\ell\ell'}$, are to be determined self-consistently.

Following HOOTON [5.35], we assume that the level scheme of \hat{H} is the same as that for H except for an approximately constant energy shift ε , at least as far as the low levels are concerned. It is also assumed that the eigenfunctions of \hat{H} and of H are similar, again an approximation which obviously fails for highly excited states. The preceding assumptions can be expressed by saying that the operator

$$\hat{V} = \phi - \hat{\phi} \quad (0.5)$$

is small in an average sense, that is, that the operator

$$H - \hat{H} - \varepsilon = \hat{V} - \varepsilon \quad (0.6)$$

has approximately degenerate eigenstates of eigenvalue zero. Writing $H = \varepsilon + \hat{H} + (\hat{V} - \varepsilon)$, we can write the density matrix $\rho(H)$ [5.44], in the following form

$$\rho(H) = e^{-\beta H} = e^{-\beta\varepsilon} \rho(\hat{H}) e^{-\beta(\hat{V} - \varepsilon)} \quad . \quad (0.7a)$$

The above assumptions require that we may approximately disregard the last factor in (0.7a). Thus

$$\rho(H) \simeq e^{-\beta\varepsilon} \rho(\hat{H}) \quad . \quad (0.7b)$$

More precisely we require that the average value of the operator $\exp[-\beta(\hat{V}-\varepsilon)]$ should be unity

$$\langle e^{-\beta(\hat{V}-\varepsilon)} \rangle_h = 1 \quad . \quad (0.8)$$

Here, $\langle \dots \rangle_h$ is the thermal average constructed according the effective harmonic Hamiltonian \hat{H} . Expanding (0.8) to first order in the operator $\hat{V}-\varepsilon$ gives

$$\varepsilon = \langle \hat{V} \rangle_h \quad . \quad (0.9)$$

Using (0.7b) and (0.9) we can write the free energy approximately as

$$F = -k_B T \ln \text{Tr}\{\rho(H)\} = \hat{F}_{\text{vib}} + \langle \hat{V} \rangle_h , \quad (0.10)$$

where

$$\hat{F}_{\text{vib}} = -k_B T \ln \text{Tr}\{\hat{\rho}(H)\} , \quad (0.11)$$

is the free energy belonging to the effective harmonic Hamiltonian \hat{H} . Substituting (0.2) and (0.4) in (0.5), we obtain from (0.10)

$$\begin{aligned} F = \hat{F}_{\text{vib}} &+ \frac{1}{2} \sum'_{\ell\ell'} \langle \varphi(\vec{r}_{\ell\ell'} + \vec{w}_{\ell\ell'}) \rangle_h \\ &- \frac{1}{4} \sum'_{\ell\ell'} \sum_{\alpha\beta} \hat{\varphi}_{\alpha\beta}(\ell\ell') \sigma_{\alpha\beta}(\ell\ell') , \end{aligned} \quad (0.12)$$

where

$$\sigma_{\alpha\beta}(\ell\ell') = \langle w_{\ell\ell'\alpha} w_{\ell\ell'\beta} \rangle_h \quad (0.13)$$

is the displacement-displacement correlation function. We now use the result that for any function $f(r)$ Taylor's theorem can be written in the form

$$f(\vec{r} + \vec{w}) = e^{\vec{w}\nabla} f(\vec{r}) , \quad (0.14)$$

where $\vec{v} = (\partial/\partial r_x, \partial/\partial r_y, \partial/\partial r_z)$. This can be verified by expanding $\exp(\vec{w}\nabla)$ in a power series. Therefore, we can write

$$\langle \varphi(\vec{r}_{\ell\ell'} + \vec{w}_{\ell\ell'}) \rangle_h = \langle e^{\vec{w}_{\ell\ell'}\nabla} \rangle_h \varphi(\vec{r}_{\ell\ell'}) . \quad (0.15)$$

For harmonic oscillators the thermal average is given by [5.45]

$$\langle e^{\vec{w}\xi} \rangle_h = e^{\frac{1}{2} \langle (\vec{w}\xi)^2 \rangle_h} . \quad (0.16)$$

Using (0.15,16) and the definition (0.13) we obtain

$$\langle \varphi(\vec{r}_{\ell\ell'} + \vec{w}_{\ell\ell'}) \rangle_h = \exp \left[\frac{1}{2} \sum_{\alpha\beta} \sigma_{\alpha\beta}(\ell\ell') d_{\alpha\beta}(\ell\ell') \right] \varphi(\vec{r}_{\ell\ell'}) , \quad (0.17)$$

where $d_{\alpha\beta}(\ell\ell') = \partial^2 / \partial r_{\ell\ell'} \alpha \partial r_{\ell\ell'} \beta$. Inserting this result in (0.12), we see that F is a function of the parameters $\hat{\varphi}_{\alpha\beta}(\ell\ell')$ and $\sigma_{\alpha\beta}(\ell\ell')$, and minimizing F with respect to these parameters we find after some rearrangements

$$\hat{\varphi}_{\alpha\beta}(\ell\ell') = \left\langle \frac{\partial^2 \varphi(\vec{r}_{\ell\ell'} + \vec{w}_{\ell\ell'})}{\partial r_{\ell\ell'} \alpha \partial r_{\ell\ell'} \beta} \right\rangle_h \quad (0.18)$$

and

$$\sigma_{\alpha\beta}(\ell\ell') = 4 \frac{\partial \hat{F}_{\text{vib}}}{\partial \hat{\varphi}_{\alpha\beta}(\ell\ell')} = 4 \sum_s \frac{\partial \hat{F}_{\text{vib}}}{\partial \hat{\omega}_s} \frac{\partial \hat{\omega}_s}{\partial \hat{\varphi}_{\alpha\beta}(\ell\ell')} . \quad (0.19)$$

\hat{F}_{vib} is obtained from (N.6) if in this expression, ω_s is replaced by $\hat{\omega}_s$, thus

$$\hat{F}_{\text{vib}} = k_B T \sum_s \ln \left(2 \sinh \frac{\hbar \hat{\omega}_s}{2k_B T} \right) . \quad (0.20)$$

Using the eigenvalue equation (5.109a) we obtain

$$\begin{aligned} & \sigma_{\alpha\beta}(\ell\ell') \\ &= \frac{\hbar}{Nm} \sum_{\vec{q}j} \hat{e}_\alpha^*(\vec{q}) \hat{e}_\beta(\vec{q}) \frac{1 - e^{i\vec{q}\vec{r}_{\ell\ell'}}}{\hat{\omega}_j(\vec{q})} \coth \frac{\hbar \hat{\omega}_j(\vec{q})}{2k_B T} . \end{aligned} \quad (0.21)$$

This result can also be derived by representing the displacement coordinates in terms of creation and annihilation operators (see Problem 5.6.5).

We are now able to calculate the quantity $D_{\ell\ell'}(\vec{Q})$ defined by (5.115), which can be written in the form

$$D_{\ell\ell'}(\vec{Q}) = \frac{1}{2} \sum_{\alpha\beta} Q_\alpha Q_\beta \sigma_{\alpha\beta}(\ell\ell') .$$

Substituting (0.21) in this expression, we immediately obtain

$$\begin{aligned} & D_{\ell\ell'}(\vec{Q}) \\ &= \frac{\hbar}{2Nm} \sum_{\vec{q}j} \frac{|\hat{Q}e_j(\vec{q})|^2}{\hat{\omega}_j(\vec{q})} (1 - e^{i\vec{q}\vec{r}_{\ell\ell'}}) \coth \frac{\hbar \hat{\omega}_j(\vec{q})}{2k_B T} . \end{aligned} \quad (0.22)$$

The equation of state for cubic crystals is obtained from $P = -(\partial F / \partial V)_T$.

From $F = -k_B T \ln \text{Tr}\{\rho(H)\}$ we obtain immediately

$$P = - \frac{\text{Tr} \left\{ \frac{\partial H}{\partial V} \rho(H) \right\}}{\text{Tr}\{\rho(H)\}} = - \left\langle \frac{\partial H}{\partial V} \right\rangle . \quad (0.23a)$$

Using the approximation (0.7b), we obtain

$$P = - \left\langle \frac{\partial H}{\partial V} \right\rangle_h . \quad (0.23b)$$

Since in $H = T_{\text{kin}} + \Phi$ the kinetic energy is independent of the volume $V = Nv_a$ and since according to (0.2), Φ can be written in the form

$$\Phi = \frac{1}{2} N \sum_\ell \varphi(\vec{r}_{0\ell} + \vec{w}_{0\ell}) , \quad (0.24)$$

we obtain

$$P = - \frac{1}{2} \sum_\ell \left\langle \frac{\partial}{\partial v_a} \varphi(\vec{r}_{0\ell} + \vec{w}_{0\ell}) \right\rangle_h . \quad (0.25)$$

For cubic Bravais lattices, we may write $\vec{r}_{0\ell} = \sum_{\alpha} \ell_{\alpha} r_{\alpha} \vec{e}_{\alpha}$ where \vec{e}_{α} are unit vectors in the x, y, and z-directions, ℓ_{α} are integers and r_{α} are suitably chosen distances [i.e., $r_{\alpha} = a$ for the simple cubic lattice and $r_{\alpha} = a/2$ for the fcc and bcc lattices (a = lattice parameter)]. The volume of the primitive unit cell is $v_a = n r_x r_y r_z$ where n is a number which depends on the type of the lattice ($n = 2$ for fcc, $n = 4$ for bcc). Using $r_{0\ell\alpha} = \ell_{\alpha} r_{\alpha}$ and $\partial v_a / \partial r_{\alpha} = v_a / r_{\alpha}$ we find

$$\begin{aligned} \frac{\partial \varphi}{\partial v_a} &= \sum_{\alpha} \frac{\partial \varphi}{\partial r_{0\ell\alpha}} \frac{\partial r_{0\ell\alpha}}{\partial v_a} = \frac{1}{v_a} \sum_{\alpha} \ell_{\alpha} r_{\alpha} \frac{\partial \varphi}{\partial r_{0\ell\alpha}} \\ &= \frac{1}{v_a} \sum_{\alpha} r_{0\ell\alpha} \frac{\partial \varphi}{\partial r_{0\ell\alpha}} = \frac{1}{v_a} \vec{r}_{0\ell} \nabla \varphi(\vec{r}_{0\ell} + \vec{w}_{0\ell}) \quad . \end{aligned}$$

Thus we obtain the result

$$PV = -\frac{1}{2} N \sum_{\ell} \langle \vec{r}_{0\ell} \nabla \varphi(\vec{r}_{0\ell} + \vec{w}_{0\ell}) \rangle_h \quad . \quad (0.26)$$

Putting $P = 0$, we obtain the equilibrium condition at zero pressure

$$\sum_{\ell} \langle \vec{r}_{0\ell} \nabla \varphi(\vec{r}_{0\ell} + \vec{w}_{0\ell}) \rangle_h = 0 \quad . \quad (0.27)$$

P) Expansion Coefficients of Anharmonic Terms

Substituting (3.74) in (5.147) the expansion coefficients of H_3 have the form

$$\begin{aligned} V(j^{\vec{q}} j_1^{\vec{q}_1} j_2^{\vec{q}_2}) &= \frac{1}{3!} \left(\frac{h}{2N} \right)^{3/2} \sum_{\substack{\kappa \kappa_1 \kappa_2 \\ \alpha \beta \gamma}} F(\kappa \kappa_1 \kappa_2 | j^{\vec{q}} j_1^{\vec{q}_1} j_2^{\vec{q}_2}) \\ &\times \sum_{\ell \ell_1 \ell_2} \Phi_{\alpha \beta \gamma}(\kappa \kappa_1 \kappa_2 | j^{\vec{q}} j_1^{\vec{q}_1} j_2^{\vec{q}_2}) e^{i[\vec{q} \vec{r}(\ell) + \vec{q}_1 \vec{r}(\ell_1) + \vec{q}_2 \vec{r}(\ell_2)]} \quad , \quad (P.1) \end{aligned}$$

where

$$\begin{aligned} F(\kappa \kappa_1 \kappa_2 | j^{\vec{q}} j_1^{\vec{q}_1} j_2^{\vec{q}_2}) &= \frac{e^{i[\vec{q} \vec{r}(\kappa) + \vec{q}_1 \vec{r}(\kappa_1) + \vec{q}_2 \vec{r}(\kappa_2)]}}{(m \kappa \kappa_1 \kappa_2)^{1/2}} \frac{e_{\alpha}(\kappa | j^{\vec{q}}) e_{\beta}(\kappa_1 | j_1^{\vec{q}_1}) e_{\gamma}(\kappa_2 | j_2^{\vec{q}_2})}{[\omega_j(\vec{q}) \omega_{j_1}(\vec{q}_1) \omega_{j_2}(\vec{q}_2)]^{1/2}} \quad . \quad (P.2) \end{aligned}$$

Putting

$$\vec{r}(\ell_1) - \vec{r}(\ell) = \vec{r}(h_1) \quad ; \quad \vec{r}(\ell_2) - \vec{r}(\ell) = \vec{r}(h_2) \quad ,$$

the last exponential factor in (P.1) becomes

$$e^{i(\vec{q} + \vec{q}_1 + \vec{q}_2) \cdot \vec{r}(\ell)} e^{i[\vec{q}_1 \cdot \vec{r}(h_1) + \vec{q}_2 \cdot \vec{r}(h_2)]} .$$

The coupling coefficients are now $\Phi_{\alpha\beta\gamma}^{(\ell \ k \ k_1 \ k_2)}$ and the sum over lattice sites is over ℓ , h_1 and h_2 . Due to the translational invariance of H_3 , we have

$$\Phi_{\alpha\beta\gamma}^{(\ell \ k \ k_1 \ k_2)} = \Phi_{\alpha\beta\gamma}^{(0 \ k \ k_1 \ k_2)} . \quad (P.3)$$

This relation is completely analogous to the relation (3.19) and can be proved in the same way. Tables of coupling parameters of third and fourth order for the simple cubic, bcc and fcc lattices are given in [5.54]. The last sum in (P.1) can, therefore, be written as

$$N \sum_{h_1 h_2} \Phi_{\alpha\beta\gamma}^{(0 \ k \ k_1 \ k_2)} e^{i[\vec{q}_1 \cdot \vec{r}(h_1) + \vec{q}_2 \cdot \vec{r}(h_2)]} \Delta(\vec{q} + \vec{q}_1 + \vec{q}_2) ,$$

where we have used (3.66). From this, it follows that

$$\begin{aligned} v_j^{\vec{q} \vec{q}_1 \vec{q}_2} &= \frac{1}{3!} \left(\frac{N}{2}\right)^{3/2} N^{-1/2} \sum_{\substack{k k_1 k_2 \\ \alpha \beta \gamma}} F_{\alpha \beta \gamma}^{(k \ k_1 \ k_2 | j \ j_1 \ j_2)} \\ &\times \sum_{h_1 h_2} \Phi_{\alpha\beta\gamma}^{(0 \ k \ k_1 \ k_2)} e^{i[\vec{q}_1 \cdot \vec{r}(h_1) + \vec{q}_2 \cdot \vec{r}(h_2)]} \Delta(\vec{q} + \vec{q}_1 + \vec{q}_2) . \end{aligned}$$

An analogous expression holds for the coefficients of H_4 .

Q) Constants and Units

General Physical Constants

Gas constant	$R = 8.31 \cdot 10^7 \text{ erg mole}^{-1} \text{K}^{-1}$
Loschmidt's number	$N_L = 6.0225 \cdot 10^{23} \text{ mole}^{-1}$
Speed of light in vacuum	$c = 2.998 \cdot 10^{10} \text{ cm s}^{-1}$

Atomic Constants

Boltzmann's constant	$k_B = 1.381 \cdot 10^{-16} \text{ erg K}^{-1}$
Planck's constant	$h = 6.626 \cdot 10^{-27} \text{ erg s}$
Planck's constant / 2π	$\hbar = 1.054 \cdot 10^{-27} \text{ erg s}$

Electron rest mass	$m = 0.911 \cdot 10^{-27} \text{ g}$
Proton rest mass	$M_p = 1.6725 \cdot 10^{-24} \text{ g}$
Neutron rest mass	$M_n = 1.6747 \cdot 10^{-24} \text{ g}$
Proton mass/electron mass	$M_p/m = 1836$
Atomic mass unit ($\equiv \frac{1}{16}$ mass of O^{16})	$1 \text{ amu} = 1.657 \cdot 10^{-24} \text{ g}$
Charge on electron	$e = 4.803 \cdot 10^{-10} \text{ esu}$ $= 1.602 \cdot 10^{-19} \text{ C}$
Bohr radius of the ground state of hydrogen	$a_0 = \frac{\hbar^2}{me^2} = 0.529 \text{ \AA}$
Rydberg's constant	$1.09737 \cdot 10^5 \text{ cm}^{-1}$

Length

Angström	$1 \text{ \AA} = 10^{-8} \text{ cm}$
Micron	$1 \text{ mu} = 10^{-4} \text{ cm}$

Energy conversion table

E	erg	J	cal	eV
1 erg =	1	10^{-7}	$2.3892 \cdot 10^{-8}$	$6.242 \cdot 10^{11}$
1 Joule =	10^7	1	$2.3892 \cdot 10^{-1}$	$6.242 \cdot 10^{18}$
1 cal =	$4.1855 \cdot 10^7$	4.1855	1	$2.613 \cdot 10^{19}$
1 eV =	$1.602 \cdot 10^{-12}$	$1.602 \cdot 10^{-19}$	$3.827 \cdot 10^{-20}$	1

From $E = hc\nu = k_B T$: $1 \text{ eV} \hat{=} 8066 \text{ cm}^{-1} \hat{=} 11605 \text{ K}$

$1 \text{ cm}^{-1} \hat{=} 1.438 \text{ K}$; $1 \text{ K} \hat{=} 0.695 \text{ cm}^{-1}$

($\hat{=}$ means: corresponds to).

Force, Force Constants and Elastic Constants

Newton	$1 \text{ N} = 1 \text{ kg ms}^{-2} = 10^5 \text{ dyn}$
dyn	$1 \text{ dyn} = 1 \text{ g cm s}^{-2}$
mdyn	$1 \text{ mdyn} = 10^{-3} \text{ dyn}$
Force constants	in dyn/cm or mdyn/\AA
Elastic constants	in dyn/cm^2

Energy E

erg	1 erg = 1 dyn cm
Joule	1 J = 1 Nm = 1 Ws

Frequency ν

Hertz	1 Hz = 1 s ⁻¹
Megahertz	1 MHz = 10 ⁶ Hz
Gigahertz	1 GHz = 10 ⁹ Hz
Terahertz	1 THz = 10 ¹² Hz

Wave Number ̃ν

= number of wavelengths λ per cm
 $\tilde{\nu} = 1/\lambda = \nu/c$, in units of cm⁻¹
 (1 THz ≈ 33.3 cm⁻¹)

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Photoemission in Solids I

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Case Studies

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