Dynamics of Crystal Lattice

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Content

Elastic Vibration of a Continuous Medium; Concept of Phonon; One-dimensional Monatomic and Diatomic Lattices; Theories of Lattice Specific Heat - Einstein Model and Debye Model.

References

Introduction to Solid State Physics – Charles Kittel
Solid State Physics – Neil W. Ashcroft, N. David Mermin
Elementary Solid State Physics: Principles and Applications – M. Ali Omar

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Phonons I. Crystal Vibrations

Chapter 5 treats the thermal properties of phonons.

	Name	Field
⟶	Electron	—
	Photon	Electromagnetic wave
	Phonon	Elastic wave
	Plasmon	Collective electron wave
	Magnon	Magnetization wave
–	Polaron	Electron + elastic deformation
–	Exciton	Polarization wave

Figure 1 Important elementary excitations in solids.

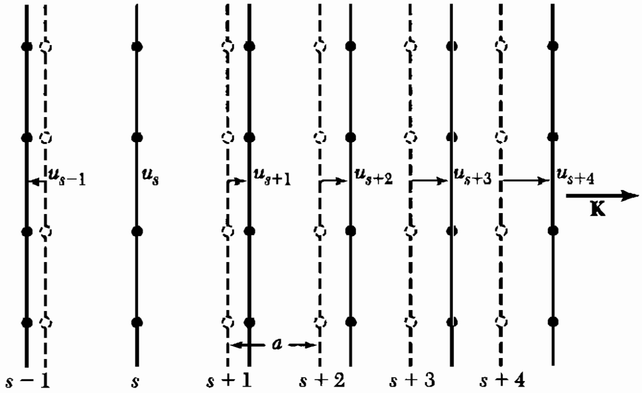

Figure 2 (Dashed lines) Planes of atoms when in equilibrium. (Solid lines) Planes of atoms when displaced as for a longitudinal wave. The coordinate u measures the displacement of the planes.

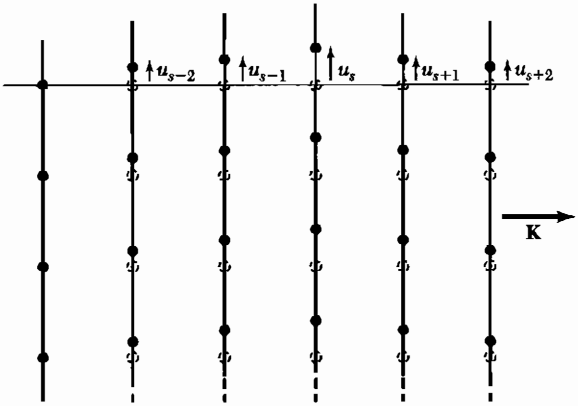

Figure 3 Planes of atoms as displaced during passage of a transverse wave.

VIBRATIONS OF CRYSTALS WITH MONATOMIC BASIS

Consider the elastic vibrations of a crystal with one atom in the primitive cell. We want to find the frequency of an elastic wave in terms of the wavevector that describes the wave and in terms of the elastic constants.

The mathematical solution is simplest in the [100], [110], and [111] propagation directions in cubic crystals. These are the directions of the cube edge, face diagonal, and body diagonal. When a wave propagates along one of these directions, entire planes of atoms move in phase with displacements either parallel or perpendicular to the direction of the wavevector. We can describe with a single coordinate u_s the displacement of the plane s from its equilibrium position. The problem is now one dimensional. For each wavevector there are three modes as solutions for u_s, one of longitudinal polarization (Fig. 2) and two of transverse polarization (Fig. 3).

We assume that the elastic response of the crystal is a linear function of the forces. That is equivalent to the assumption that the elastic energy is a quadratic function of the relative displacement of any two points in the crystal. Terms in the energy that are linear in the displacements will vanish in equilibrium—see the minimum in Fig. 3.6. Cubic and higher-order terms may be neglected for sufficiently small elastic deformations.

We assume that the force on the plane s caused by the displacement of the plane $s + p$ is proportional to the difference $u_{s+p} - u_s$ of their displacements. For brevity we consider only nearest-neighbor interactions, with $p = \pm 1$. The total force on s from planes $s \pm 1$:

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s) \ . \tag{1}$$

This expression is linear in the displacements and is of the form of Hooke's law.

The constant C is the **force constant** between nearest-neighbor planes and will differ for longitudinal and transverse waves. It is convenient hereafter to regard C as defined for one atom of the plane, so that F_s is the force on one atom in the plane s.

The equation of motion of an atom in the plane s is

$$M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s) \ , \tag{2}$$

where M is the mass of an atom. We look for solutions with all displacements having the time dependence $\exp(-i\omega t)$. Then $d^2u_s/dt^2 = -\omega^2 u_s$, and (2) becomes

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s) \ . \tag{3}$$

This is a difference equation in the displacements u and has traveling wave solutions of the form:

$$u_{s\pm 1} = u \exp(isKa) \exp(\pm iKa) \ , \tag{4}$$

where a is the spacing between planes and K is the wavevector. The value to use for a will depend on the direction of K.

With (4), we have from (3):

$$-\omega^2 Mu \exp(isKa) = Cu\{\exp[i(s+1)Ka] + \exp[i(s-1)Ka] - 2\exp(isKa)\} \ . \tag{5}$$

We cancel $u \exp(isKa)$ from both sides, to leave

$$\omega^2 M = -C[\exp(iKa) + \exp(-iKa) - 2] \ . \tag{6}$$

With the identity $2 \cos Ka = \exp(iKa) + \exp(-iKa)$, we have the **dispersion relation** $\omega(K)$.

$$\omega^2 = (2C/M)(1 - \cos Ka) \ . \tag{7}$$

The boundary of the first Brillouin zone lies at $K = \pm\pi/a$. We show from (7) that the slope of ω versus K is zero at the zone boundary:

$$d\omega^2/dK = (2Ca/M) \sin Ka = 0 \tag{8}$$

at $K = \pm\pi/a$, for here $\sin Ka = \sin(\pm\pi) = 0$. The special significance of phonon wavevectors that lie on the zone boundary is developed in (12) below.

By a trigonometric identity, (7) may be written as

$$\omega^2 = (4C/M) \sin^2 \tfrac{1}{2} Ka \ ; \qquad \omega = (4C/M)^{1/2} |\sin \tfrac{1}{2} Ka| \ . \tag{9}$$

A plot of ω versus K is given in Fig. 4.

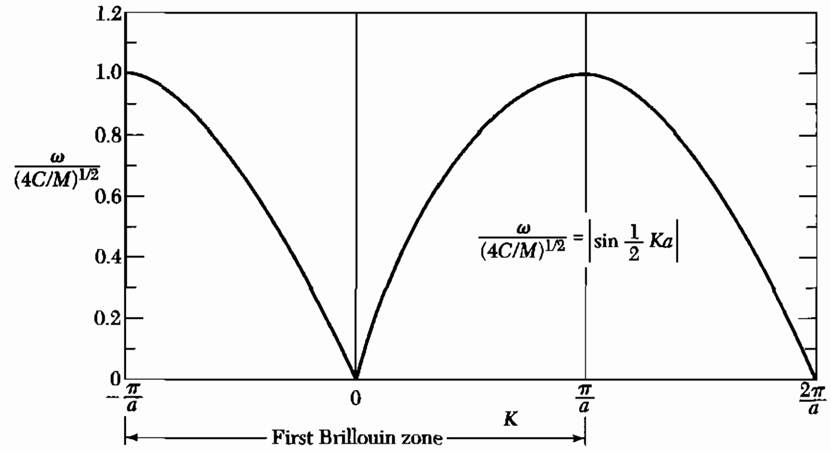

Figure 4 Plot of ω versus K. The region of $K \ll 1/a$ or $\lambda \gg a$ corresponds to the continuum approximation; here ω is directly proportional to K.

First Brillouin Zone

What range of K is physically significant for elastic waves? Only those in the first Brillouin zone. From (4) the ratio of the displacements of two successive planes is given by

$$\frac{u_{s+1}}{u_s} = \frac{u \exp[i(s+1)Ka]}{u \exp(isKa)} = \exp(iKa) \ . \tag{10}$$

The range $-\pi$ to $+\pi$ for the phase Ka covers all independent values of the exponential.

The range of independent values of K is specified by

$$-\pi < Ka \leq \pi \ , \qquad \text{or} \qquad -\frac{\pi}{a} < K \leq \frac{\pi}{a} \ .$$

This range is the first Brillouin zone of the linear lattice, as defined in Chapter 2. The extreme values are $K_{\max} = \pm\pi/a$. Values of K outside of the first Brillouin zone (Fig. 5) merely reproduce lattice motions described by values within the limits $\pm\pi/a$.

We may treat a value of K outside these limits by subtracting the integral multiple of $2\pi/a$ that will give a wavevector inside these limits. Suppose K lies outside the first zone, but a related wavevector K' defined $K' = K - 2\pi n/a$ lies within the first zone, where n is an integer. Then the displacement ratio (10) becomes

$$u_{s+1}/u_s = \exp(iKa) \equiv \exp(i2\pi n) \exp[i(Ka - 2\pi n)] \equiv \exp(iK'a) \ , \tag{11}$$

because $\exp(i2\pi n) = 1$. Thus the displacement can always be described by a wavevector within the first zone. We note that $2\pi n/a$ is a reciprocal lattice vector because $2\pi/a$ is a reciprocal lattice vector. Thus by subtraction of an appropriate reciprocal lattice vector from K, we always obtain an equivalent wavevector in the first zone.

At the boundaries $K_{\max} = \pm\pi/a$ of the Brillouin zone the solution $u_s = u \exp(isKa)$ does not represent a traveling wave, but a standing wave. At the zone boundaries $sK_{\max}a = \pm s\pi$, whence

$$u_s = u \exp(\pm is\pi) = u\,(-1)^s \ . \tag{12}$$

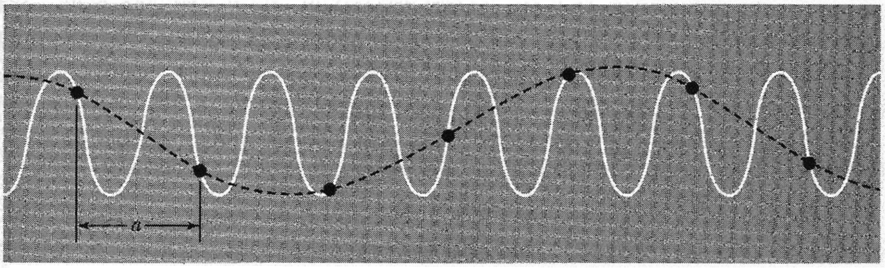

Figure 5 The wave represented by the solid curve conveys no information not given by the dashed curve. Only wavelengths longer than $2a$ are needed to represent the motion.

This is a standing wave: alternate atoms oscillate in opposite phases, because $u_s = \pm 1$ according to whether s is an even or an odd integer. The wave moves neither to the right nor to the left.

This situation is equivalent to Bragg reflection of x-rays: when the Bragg condition is satisfied a traveling wave cannot propagate in a lattice, but through successive reflections back and forth, a standing wave is set up.

The critical value $K_{\max} = \pm\pi/a$ found here satisfies the Bragg condition $2d \sin\theta = n\lambda$: we have $\theta = \frac{1}{2}\pi$, $d = a$, $K = 2\pi/\lambda$, $n = 1$, so that $\lambda = 2a$. With x-rays it is possible to have n equal to other integers besides unity because the amplitude of the electromagnetic wave has a meaning in the space between atoms, but the displacement amplitude of an elastic wave usually has a meaning only at the atoms themselves.

Group Velocity

The transmission velocity of a wave packet is the **group velocity**, given as

$$v_g = d\omega/dK \ ,$$

or

$$\mathbf{v}_g = \mathrm{grad}_{\mathbf{K}}\, \omega(\mathbf{K}) \ , \qquad (13)$$

the gradient of the frequency with respect to $\mathbf{K}$. This is the velocity of energy propagation in the medium.

With the particular dispersion relation (9), the group velocity (Fig. 6) is

$$v_g = (Ca^2/M)^{1/2} \cos \tfrac{1}{2} Ka \ . \qquad (14)$$

This is zero at the edge of the zone where $K = \pi/a$. Here the wave is a standing wave, as in (12), and we expect zero net transmission velocity for a standing wave.

Long Wavelength Limit

When $Ka \ll 1$ we expand $\cos Ka \cong 1 - \frac{1}{2}(Ka)^2$, so that the dispersion relation (7) becomes

$$\omega^2 = (C/M)K^2a^2 \ . \qquad (15)$$

The result that the frequency is directly proportional to the wavevector in the long wavelength limit is equivalent to the statement that the velocity of sound is independent of frequency in this limit. Thus $v = \omega/K$, exactly as in the continuum theory of elastic waves—in the continuum limit $Ka \ll 1$.

Derivation of Force Constants from Experiment

In metals the effective forces may be of quite long range and are carried from ion to ion through the conduction electron sea. Interactions have been found between planes of atoms separated by as many as 20 planes. We can make a statement about the range of the forces from the observed experimental

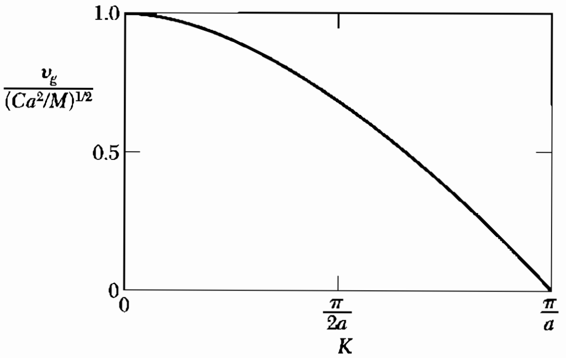

Figure 6 Group velocity v_g versus K, for model of Fig. 4. At the zone boundary $K = \pi/a$ the group velocity is zero.

dispersion relation for ω. The generalization of the dispersion relation (7) to p nearest planes is easily found to be

$$\omega^2 = (2/M) \sum_{p>0} C_p(1 - \cos pKa) \ . \tag{16a}$$

We solve for the interplanar force constants C_p by multiplying both sides by cos rKa, where r is an integer, and integrating over the range of independent values of K:

$$\begin{aligned} M\int_{-\pi/a}^{\pi/a} dK\, \omega_K^2 \cos rKa &= 2\sum_{p>0} C_p \int_{-\pi/a}^{\pi/a} dK\,(1 - \cos pKa)\cos rKa \\ &= -2\pi C_r/a \ . \end{aligned} \tag{16b}$$

The integral vanishes except for $p = r$. Thus

$$C_p = -\frac{Ma}{2\pi}\int_{-\pi/a}^{\pi/a} dK\, \omega_K^2 \cos pKa \tag{17}$$

gives the force constant at range pa, for a structure with a monatomic basis.

TWO ATOMS PER PRIMITIVE BASIS

The phonon dispersion relation shows new features in crystals with two or more atoms per primitive basis. Consider, for example, the NaCl or diamond structures, with two atoms in the primitive cell. For each polarization mode in a given propagation direction the dispersion relation ω versus K develops two branches, known as the acoustical and optical branches, as in Fig. 7. We have longitudinal LA and transverse acoustical TA modes, and longitudinal LO and transverse optical TO modes.

If there are p atoms in the primitive cell, there are $3p$ branches to the dispersion relation: 3 acoustical branches and $3p - 3$ optical branches. Thus germanium (Fig. 8a) and KBr (Fig. 8b), each with two atoms in a primitive cell, have six branches: one LA, one LO, two TA, and two TO.

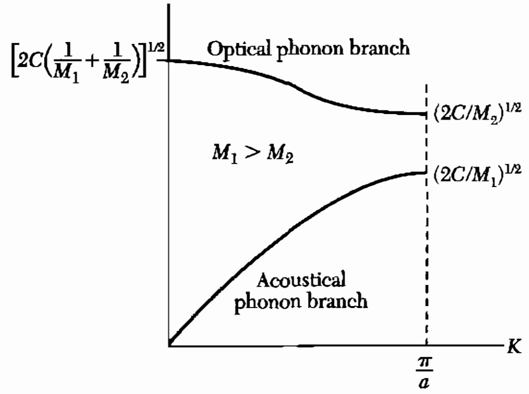

Figure 7 Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K = 0$ and $K = K_{\max} = \pi/a$. The lattice constant is a.

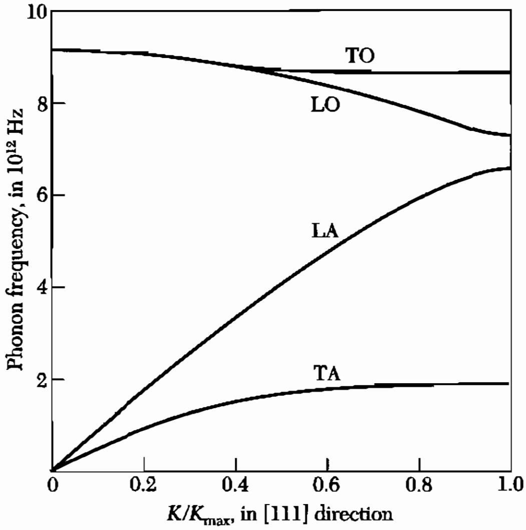

Figure 8a Phonon dispersion relations in the [111] direction in germanium at 80 K. The two TA phonon branches are horizontal at the zone boundary position, $K_{\max} = (2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The LO and TO branches coincide at $K = 0$; this also is a consequence of the crystal symmetry of Ge. The results were obtained with neutron inelastic scattering by G. Nilsson and G. Nelin.

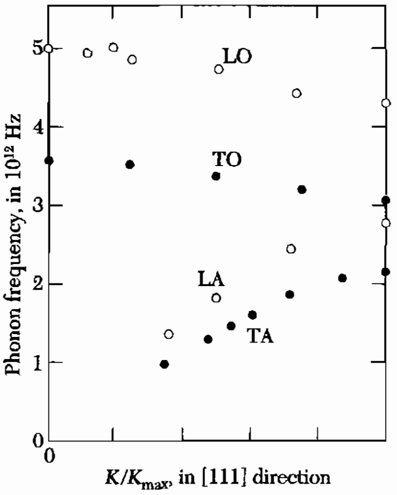

Figure 8b Dispersion curves in the [111] direction in KBr at 90 K, after A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran. The extrapolation to $K = 0$ of the TO, LO branches are called ω_T, ω_L.

The numerology of the branches follows from the number of degrees of freedom of the atoms. With p atoms in the primitive cell and N primitive cells, there are pN atoms. Each atom has three degrees of freedom, one for each of the x, y, z directions, making a total of $3pN$ degrees of freedom for the crystal. The number of allowed K values in a single branch is just N for one Brillouin zone.[1] Thus the

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[1] We show in Chapter 5 by application of periodic boundary conditions to the modes of the crystal of volume V that there is one $\mathbf{K}$ value in the volume $(2\pi)^3/V$ in Fourier space. The volume of a Brillouin zone is $(2\pi)^3/V_c$, where V_c is the volume of a crystal primitive cell. Thus the number of allowed $\mathbf{K}$ values in a Brillouin zone is V/V_c, which is just N, the number of primitive cells in the crystal.

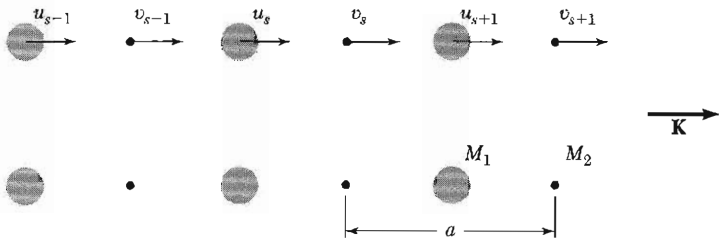


Figure 9 A diatomic crystal structure with masses M_1, M_2 connected by force constant C between adjacent planes. The displacements of atoms M_1 are denoted by $u_{s-1}, u_s, u_{s+1}, \ldots$, and of atoms M_2 by v_{s-1}, v_s, v_{s+1}. The repeat distance is a in the direction of the wavevector K. The atoms are shown in their undisplaced positions.

LA and the two TA branches have a total of $3N$ modes, thereby accounting for $3N$ of the total degrees of freedom. The remaining $(3p - 3)N$ degrees of freedom are accommodated by the optical branches.

We consider a cubic crystal where atoms of mass M_1 lie on one set of planes and atoms of mass M_2 lie on planes interleaved between those of the first set (Fig. 9). It is not essential that the masses be different, but either the force constants or the masses will be different if the two atoms of the basis are in nonequivalent sites. Let a denote the repeat distance of the lattice in the direction normal to the lattice planes considered. We treat waves that propagate in a symmetry direction such that a single plane contains only a single type of ion; such directions are [111] in the NaCl structure and [100] in the CsCl structure.

We write the equations of motion under the assumption that each plane interacts only with its nearest-neighbor planes and that the force constants are identical between all pairs of nearest-neighbor planes. We refer to Fig. 9 to obtain

$$\begin{aligned} M_1 \frac{d^2 u_s}{dt^2} &= C(v_s + v_{s-1} - 2u_s) \ ; \\ M_2 \frac{d^2 v_s}{dt^2} &= C(u_{s+1} + u_s - 2v_s) \ . \end{aligned} \tag{18}$$

We look for a solution in the form of a traveling wave, now with different amplitudes u, v on alternate planes:

$$u_s = u \exp(isKa)\exp(-i\omega t) \ ; \qquad v_2 = v \exp(isKa)\exp(-i\omega t) \ . \tag{19}$$

We define a in Fig. 9 as the distance between nearest identical planes, not nearest-neighbor planes.

On substitution of (19) in (18) we have

$$\begin{aligned} -\omega^2 M_1 u &= Cv[1 + \exp(-iKa)] - 2Cu \ ; \\ -\omega^2 M_2 v &= Cu[\exp(iKa) + 1] - 2Cv \ . \end{aligned} \tag{20}$$

The homogeneous linear equations have a solution only if the determinant of the coefficients of the unknowns u, v vanishes:

$$\begin{vmatrix} 2C - M_1\omega^2 & -C[1+\exp(iKa)] \\ -C[1+\exp(iKa)] & 2C - M_2\omega^2 \end{vmatrix} = 0 \ , \tag{21}$$

or

$$M_1M_2\omega^4 - 2C(M_1+M_2)\omega^2 + 2C^2(1-\cos Ka) = 0 \ . \tag{22}$$

We can solve this equation exactly for ω^2, but it is simpler to examine the limiting cases $Ka \ll 1$ and $Ka = \pm\pi$ at the zone boundary. For small Ka we have $\cos Ka \cong 1 - \frac{1}{2}K^2a^2 + \ldots$, and the two roots are

$$\omega^2 \cong 2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \qquad \text{(optical branch)} \ ; \tag{23}$$

$$\omega^2 \cong \frac{\frac{1}{2}C}{M_1+M_2}K^2a^2 \qquad \text{(acoustical branch)} \ . \tag{24}$$

The extent of the first Brillouin zone is $-\pi/a \leq K \leq \pi/a$, where a is the repeat distance of the lattice. At $K_{max} = \pm\pi/a$ the roots are

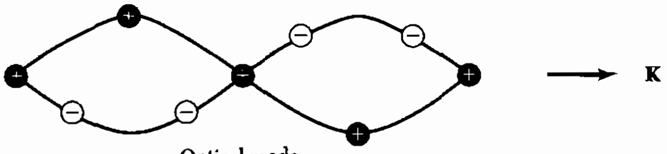
$$\omega^2 = 2C/M_1 \ ; \qquad \omega^2 = 2C/M_2 \ . \tag{25}$$

The dependence of ω on K is shown in Fig. 7 for $M_1 > M_2$.

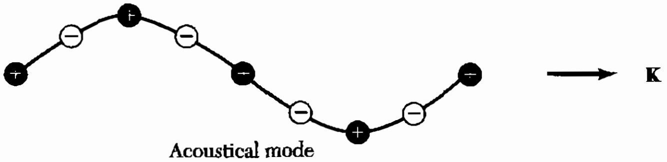
The particle displacements in the transverse acoustical (TA) and transverse optical (TO) branches are shown in Fig. 10. For the optical branch at $K = 0$ we find, on substitution of (23) in (20),

$$\frac{u}{v} = -\frac{M_2}{M_1} \ . \tag{26}$$

The atoms vibrate against each other, but their center of mass is fixed. If the two atoms carry opposite charges, as in Fig. 10, we may excite a motion of this



Optical mode



Acoustical mode

Figure 10 Transverse optical and transverse acoustical waves in a diatomic linear lattice, illustrated by the particle displacements for the two modes at the same wavelength.

type with the electric field of a light wave, so that the branch is called the optical branch. At a general K the ratio u/v will be complex, as follows from either of the equations (20). Another solution for the amplitude ratio at small K is $u = v$, obtained as the $K = 0$ limit of (24). The atoms (and their center of mass) move together, as in long wavelength acoustical vibrations, whence the term acoustical branch.

Wavelike solutions do not exist for certain frequencies, here between $(2C/M_1)^{1/2}$ and $(2C/M_2)^{1/2}$. This is a characteristic feature of elastic waves in polyatomic lattices. There is a frequency gap at the boundary $K_{\max} = \pm\pi/a$ of the first Brillouin zone.

QUANTIZATON OF ELASTIC WAVES

The energy of a lattice vibration is quantized. The quantum of energy is called a **phonon** in analogy with the photon of the electromagnetic wave. The energy of an elastic mode of angular frequency ω is

$$\epsilon = (n + \tfrac{1}{2})\hbar\omega \tag{27}$$

when the mode is excited to quantum number n; that is, when the mode is occupied by n phonons. The term $\frac{1}{2}\hbar\omega$ is the zero point energy of the mode. It occurs for both phonons and photons as a consequence of their equivalence to a quantum harmonic oscillator of frequency ω, for which the energy eigenvalues are also $(n + \frac{1}{2})\hbar\omega$. The quantum theory of phonons is developed in Appendix C.

We can quantize the mean square phonon amplitude. Consider the standing wave mode of amplitude

$$u = u_0 \cos Kx \cos \omega t \ .$$

Here u is the displacement of a volume element from its equilibrium position at x in the crystal. The energy in the mode, as in any harmonic oscillator, is half kinetic energy and half potential energy, when averaged over time. The kinetic energy density is $\frac{1}{2}\rho(\partial u/\partial t)^2$, where ρ is the mass density. In a crystal of volume V, the volume integral of the kinetic energy is $\frac{1}{4}\rho V\omega^2 u_0^2 \sin^2 \omega t$. The time average kinetic energy is

$$\tfrac{1}{8}\rho V\omega^2 u_0^2 = \tfrac{1}{2}(n + \tfrac{1}{2})\hbar\omega \ , \tag{28}$$

because $\langle\sin^2 \omega t\rangle = \frac{1}{2}$. The square of the amplitude of the mode is

$$u_0^2 = 4(n + \tfrac{1}{2})\hbar/\rho V\omega \ . \tag{29}$$

This relates the displacement in a given mode to the phonon occupancy n of the mode.

What is the sign of ω? The equations of motion such as (2) are equations for ω^2, and if this is positive then ω can have either sign, + or −. But the energy of a phonon must be positive, so it is conventional and suitable to view ω as positive. If the crystal structure is unstable, then ω^2 will be negative and ω will be imaginary.

PHONON MOMENTUM

A phonon of wavevector K will interact with particles such as photons, neutrons, and electrons as if it had a momentum $\hbar K$. However, a phonon does not carry physical momentum.

The reason that phonons on a lattice do not carry momentum is that a phonon coordinate (except for $K = 0$) involves relative coordinates of the atoms. Thus in an H_2 molecule the internuclear vibrational coordinate $\mathbf{r}_1 - \mathbf{r}_2$ is a relative coordinate and does not carry linear momentum; the center of mass coordinate $\frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ corresponds to the uniform mode $K = 0$ and can carry linear momentum.

In crystals there exist wavevector selection rules for allowed transitions between quantum states. We saw in Chapter 2 that the elastic scattering of an x-ray photon by a crystal is governed by the wavevector selection rule

$$\mathbf{k}' = \mathbf{k} + \mathbf{G} \ , \tag{30}$$

where $\mathbf{G}$ is a vector in the reciprocal lattice, $\mathbf{k}$ is the wavevector of the incident photon, and $\mathbf{k}'$ is the wavevector of the scattered photon. In the reflection process the crystal as a whole will recoil with momentum $-\hbar\mathbf{G}$, but this uniform mode momentum is rarely considered explicitly.

Equation (30) is an example of the rule that the total wavevector of interacting waves is conserved in a periodic lattice, with the possible addition of a reciprocal lattice vector $\mathbf{G}$. The true momentum of the whole system always is rigorously conserved. If the scattering of the photon is inelastic, with the creation of a phonon of wavevector $\mathbf{K}$, then the wavevector selection rule becomes

$$\mathbf{k}' + \mathbf{K} = \mathbf{k} + \mathbf{G} \ . \tag{31}$$

If a phonon $\mathbf{K}$ is absorbed in the process, we have instead the relation

$$\mathbf{k}' = \mathbf{k} + \mathbf{K} + \mathbf{G} \ . \tag{32}$$

Relations (31) and (32) are the natural extensions of (30).

INELASTIC SCATTERING BY PHONONS

Phonon dispersion relations $\omega(\mathbf{K})$ are most often determined experimentally by the inelastic scattering of neutrons with the emission or absorption of a phonon. A neutron sees the crystal lattice chiefly by interaction with the nuclei

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Phonons II. Thermal Properties

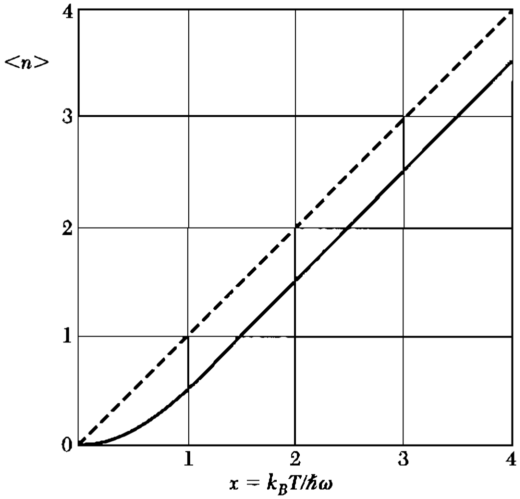

Figure 1 Plot of Planck distribution function. At high temperatures the occupancy of a state is approximately linear in the temperature. The function $\langle n \rangle + \frac{1}{2}$, which is not plotted, approaches the dashed line as asymptote at high temperatures.

CHAPTER 5: PHONONS II. THERMAL PROPERTIES

We discuss the heat capacity of a phonon gas and then the effects of anharmonic lattice interactions on the phonons and on the crystal.

PHONON HEAT CAPACITY

By heat capacity we shall usually mean the heat capacity at constant volume, which is more fundamental than the heat capacity at constant pressure, which is what the experiments determine.[1] The heat capacity at constant volume is defined as $C_V \equiv (\partial U/\partial T)_V$ where U is the energy and T the temperature.

The contribution of the phonons to the heat capacity of a crystal is called the lattice heat capacity and is denoted by C_{lat}. The total energy of the phonons at a temperature $\tau (\equiv k_B T)$ in a crystal may be written as the sum of the energies over all phonon modes, here indexed by the wavevector K and polarization index p:

$$U_{\text{lat}} = \sum_K \sum_p U_{K,p} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar \omega_{K,p} \ , \tag{1}$$

where $\langle n_{K,p} \rangle$ is the thermal equilibrium occupancy of phonons of wavevector K and polarization p. The form of $\langle n_{K,p} \rangle$ is given by the Planck distribution function:

$$\langle n \rangle = \frac{1}{\exp(\hbar\omega/\tau) - 1} \ , \tag{2}$$

where the $\langle \cdots \rangle$ denotes the average in thermal equilibrium. A graph of $\langle n \rangle$ is given in Fig. 1.

Planck Distribution

Consider a set of identical harmonic oscillators in thermal equilibrium. The ratio of the number of oscillators in their $(n+1)$th quantum state of excitation to the number in the nth quantum state is

$$N_{n+1}/N_n = \exp(-\hbar\omega/\tau) \ , \qquad \tau \equiv k_B T \ , \tag{3}$$

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[1] A thermodynamic relation gives $C_p - C_V = 9\alpha^2 BVT$, where α is the temperature coefficient of linear expansion, V the volume, and B the bulk modulus. The fractional difference between C_p and C_V is usually small in solids and often may be neglected. As $T \to 0$ we see that $C_p \to C_V$, provided α and B are constant.

by use of the Boltzmann factor. Thus the fraction of the total number of oscillators in the nth quantum state is

$$\frac{N_n}{\sum\limits_{s=0}^{\infty} N_s} = \frac{\exp(-n\hbar\omega/\tau)}{\sum\limits_{s=0}^{\infty}\exp(-s\hbar\omega/\tau)} \ . \tag{4}$$

We see that the average excitation quantum number of an oscillator is

$$\langle n \rangle = \frac{\sum\limits_{s} s\exp(-s\hbar\omega/\tau)}{\sum\limits_{s}\exp(-s\hbar\omega/\tau)} \ . \tag{5}$$

The summations in (5) are

$$\sum_s x^s = \frac{1}{1-x} \ ; \qquad \sum_s s x^s = x\frac{d}{dx}\sum_s x^s = \frac{x}{(1-x)^2} \ , \tag{6}$$

with $x = \exp(-\hbar\omega/\tau)$. Thus we may rewrite (5) as the Planck distribution:

$$\langle n \rangle = \frac{x}{1-x} = \frac{1}{\exp(\hbar\omega/\tau) - 1} \ . \tag{7}$$

Normal Mode Enumeration

The energy of a collection of oscillators of frequencies $\omega_{K,p}$ in thermal equilibrium is found from (1) and (2):

$$U = \sum_K \sum_p \frac{\hbar\omega_{K,p}}{\exp(\hbar\omega_{K,p}/\tau) - 1} \ . \tag{8}$$

It is usually convenient to replace the summation over K by an integral. Suppose that the crystal has $D_p(\omega)d\omega$ modes of a given polarization p in the frequency range ω to $\omega + d\omega$. Then the energy is

$$U = \sum_p \int d\omega\, D_p(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1} \ . \tag{9}$$

The lattice heat capacity is found by differentiation with respect to temperature. Let $x = \hbar\omega/\tau = \hbar\omega/k_BT$: then $\partial U/\partial T$ gives

$$C_{\text{lat}} = k_B \sum_p \int d\omega\, D_p(\omega) \frac{x^2 \exp x}{(\exp x - 1)^2} \ . \tag{10}$$

The central problem is to find $D(\omega)$, the number of modes per unit frequency range. This function is called the density of modes or, more often, density of states.

Density of States in One Dimension

Consider the boundary value problem for vibrations of a one-dimensional line (Fig. 2) of length L carrying $N + 1$ particles at separation a. We suppose

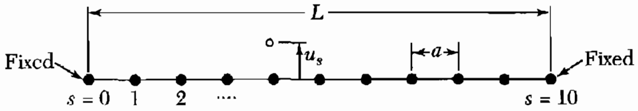


Figure 2 Elastic line of $N + 1$ atoms, with $N = 10$, for boundary conditions that the end atoms $s = 0$ and $s = 10$ are fixed. The particle displacements in the normal modes for either longitudinal or transverse displacements are of the form $u_s \propto \sin sKa$. This form is automatically zero at the atom at the end $s = 0$, and we choose K to make the displacement zero at the end $s = 10$.

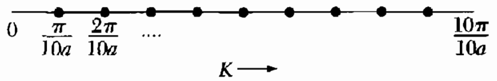


Figure 3 The boundary condition $\sin sKa = 0$ for $s = 10$ can be satisfied by choosing $K = \pi/10a$, $2\pi/10a, \ldots, 9\pi/10a$, where $10a$ is the length L of the line. The present figure is in K space. The dots are not atoms but are the allowed values of K. Of the $N + 1$ particles on the line, only $N - 1$ are allowed to move, and their most general motion can be expressed in terms of the $N - 1$ allowed values of K. *This quantization of K has nothing to do with quantum mechanics but follows classically from the boundary conditions that the end atoms be fixed.*

that the particles $s = 0$ and $s = N$ at the ends of the line are held fixed. Each normal vibrational mode of polarization p has the form of a standing wave, where u_s is the displacement of the particle s:

$$u_s = u(0) \exp(-i\omega_{K,p}t) \sin sKa \ , \tag{11}$$

where $\omega_{K,p}$ is related to K by the appropriate dispersion relation.

As in Fig. 3, the wavevector K is restricted by the fixed-end boundary conditions to the values

$$K = \frac{\pi}{L} \ , \ \frac{2\pi}{L} \ , \ \frac{3\pi}{L} \ , \ldots, \ \frac{(N-1)\pi}{L} \ . \tag{12}$$

The solution for $K = \pi/L$ has

$$u_s \propto \sin (s\pi a/L) \tag{13}$$

and vanishes for $s = 0$ and $s = N$ as required.

The solution for $K = N\pi/L = \pi/a = K_{\max}$ has $u_s \propto \sin s\pi$; this permits no motion of any atom, because $\sin s\pi$ vanishes at each atom. Thus there are $N - 1$ allowed independent values of K in (12). This number is equal to the number of particles allowed to move. Each allowed value of K is associated with a standing wave. For the one-dimensional line there is one mode for each interval $\Delta K = \pi/L$, so that the number of modes per unit range of K is L/π for $K \leq \pi/a$, and 0 for $K > \pi/a$.

There are three polarizations p for each value of K: in one dimension two of these are transverse and one longitudinal. In three dimensions the polarizations are this simple only for wavevectors in certain special crystal directions.

Another device for enumerating modes is equally valid. We consider the medium as unbounded, but require that the solutions be periodic over a large

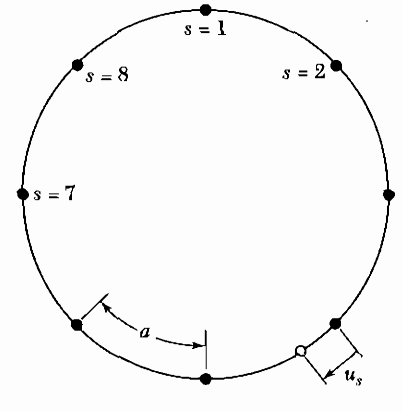


Figure 4 Consider N particles constrained to slide on a circular ring. The particles can oscillate if connected by elastic springs. In a normal mode the displacement u_s of atom s will be of the form sin sKa or cos sKa: these are independent modes. By the geometrical periodicity of the ring the boundary condition is that $u_{N+s} = u_s$ for all s, so that NKa must be an integral multiple of 2π. For $N = 8$ the allowed independent values of K are 0, $2\pi/8a$, $4\pi/8a$, $6\pi/8a$, and $8\pi/8a$. The value $K = 0$ is meaningless for the sine form, because $\sin s0a = 0$. The value $8\pi/8a$ has a meaning only for the cosine form, because $\sin (s8\pi a/8a) = \sin s\pi = 0$. The three other values of K are allowed for both the sine and cosine modes, giving a total of eight allowed modes for the eight particles. Thus the periodic boundary condition leads to one allowed mode per particle, exactly as for the fixed-end boundary condition of Fig. 3. If we had taken the modes in the complex form $\exp(isKa)$, the periodic boundary condition would lead to the eight modes with $K = 0$, $\pm 2\pi/Na$, $\pm 4\pi/Na$, $\pm 6\pi/Na$, and $8\pi/Na$, as in Eq. (14).

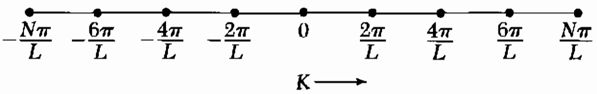


Figure 5 Allowed values of wavevector K for periodic boundary conditions applied to a linear lattice of periodicity $N = 8$ atoms on a line of length L. The $K = 0$ solution is the uniform mode. The special points $\pm N\pi/L$ represent only a single solution because $\exp(i\pi s)$ is identical to $\exp(-i\pi s)$; thus there are eight allowed modes, with displacements of the sth atom proportional to 1, $\exp(\pm i\pi s/4)$, $\exp(\pm i\pi s/2)$, $\exp(\pm i3\pi s/4)$, $\exp(i\pi s)$.

distance L, so that $u(sa) = u(sa + L)$. The method of **periodic boundary conditions** (Figs. 4 and 5) does not change the physics of the problem in any essential respect for a large system. In the running wave solution $u_s = u(0)\exp[i(sKa - \omega_K t)]$ the allowed values of K are

$$K = 0\ , \quad \pm\frac{2\pi}{L}\ , \quad \pm\frac{4\pi}{L}\ , \quad \pm\frac{6\pi}{L}\ , \ldots, \ \frac{N\pi}{L}\ . \tag{14}$$

This method of enumeration gives the same number of modes (one per mobile atom) as given by (12), but we have now both plus and minus values of K, with the interval $\Delta K = 2\pi/L$ between successive values of K. For periodic boundary conditions, the number of modes per unit range of K is $L/2\pi$ for $-\pi/a \le K \le \pi/a$, and 0 otherwise. The situation in a two-dimensional lattice is portrayed in Fig. 6.

We need to know $D(\omega)$, the number of modes per unit frequency range for a given polarization. The number of modes $D(\omega)\,d\omega$ in $d\omega$ at ω is given in one dimension by

$$D_1(\omega)\,d\omega = \frac{L}{\pi}\frac{dK}{d\omega}d\omega = \frac{L}{\pi}\cdot\frac{d\omega}{d\omega/dK}\ . \tag{15}$$

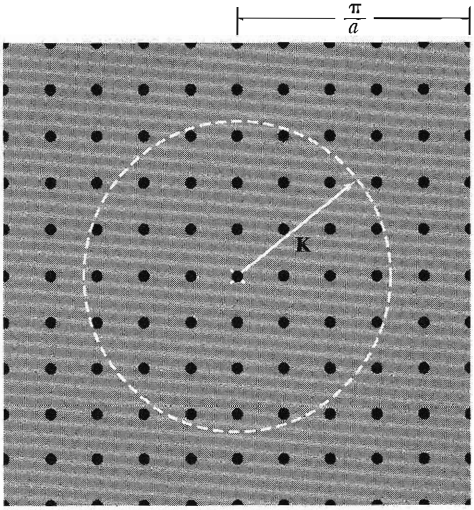


Figure 6 Allowed values in Fourier space of the phonon wavevector K for a square lattice of lattice constant a, with periodic boundary conditions applied over a square of side $L = 10a$. The uniform mode is marked with a cross. There is one allowed value of K per area $(2\pi/10a)^2 = (2\pi/L)^2$, so that within the circle of area πK^2 the smoothed number of allowed points is $\pi K^2(L/2\pi)^2$.

We can obtain the group velocity $d\omega/dK$ from the dispersion relation ω versus K. There is a singularity in $D_1(\omega)$whenever the dispersion relation $\omega(K)$ is horizontal; that is, whenever the group velocity is zero.

Density of States in Three Dimensions

We apply periodic boundary conditions over N^3 primitive cells within a cube of side L, so that $\mathbf{K}$ is determined by the condition

$$\exp[i(K_x x + K_y y + K_z z)] \equiv \exp\{i[K_x(x + L) + K_y(y + L) + K_z(z + L)]\} \ , \tag{16}$$

whence

$$K_x, K_y, K_z = 0 \ ; \quad \pm\frac{2\pi}{L} \ ; \quad \pm\frac{4\pi}{L} \ ; \quad \cdots ; \quad \frac{N\pi}{L} \ . \tag{17}$$

Therefore, there is one allowed value of $\mathbf{K}$ per volume $(2\pi/L)^3$ in $\mathbf{K}$ space, or

$$\left(\frac{L}{2\pi}\right)^3 = \frac{V}{8\pi^3} \tag{18}$$

allowed values of $\mathbf{K}$ per unit volume of $\mathbf{K}$ space, for each polarization and for each branch. The volume of the specimen is $V = L^3$.

The total number of modes with wavevector less than K is found from (18) to be $(L/2\pi)^3$ times the volume of a sphere of radius K. Thus

$$N = (L/2\pi)^3(4\pi K^3/3) \tag{19}$$

for each polarization type. The density of states for each polarization is

$$D(\omega) = dN/d\omega = (VK^2/2\pi^2)(dK/d\omega) \ . \tag{20}$$

Debye Model for Density of States

In the Debye approximation the velocity of sound is taken as constant for each polarization type, as it would be for a classical elastic continuum. The dispersion relation is written as

$$\omega = vK \ , \tag{21}$$

with v the constant velocity of sound.

The density of states (20) becomes

$$D(\omega) = V\omega^2/2\pi^2 v^3 \ . \tag{22}$$

If there are N primitive cells in the specimen, the total number of acoustic phonon modes is N. A cutoff frequency ω_D is determined by (19) as

$$\omega_D^3 = 6\pi^2 v^3 N/V \ . \tag{23}$$

To this frequency there corresponds a cutoff wavevector in **K** space:

$$K_D = \omega_D/v = (6\pi^2 N/V)^{1/3} \ . \tag{24}$$

On the Debye model we do not allow modes of wavevector larger than K_D. The number of modes with $K \leq K_D$ exhausts the number of degrees of freedom of a monatomic lattice.

The thermal energy (9) is given by

$$U = \int d\omega\, D(\omega)\langle n(\omega)\rangle\hbar\omega = \int_0^{\omega_D} d\omega \left(\frac{V\omega^2}{2\pi^2 v^3}\right)\left(\frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}\right) , \tag{25}$$

for each polarization type. For brevity we assume that the phonon velocity is independent of the polarization, so that we multiply by the factor 3 to obtain

$$U = \frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\, \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} = \frac{3Vk_B^4T^4}{2\pi^2 v^3\hbar^3}\int_0^{x_D} dx\, \frac{x^3}{e^x - 1} , \tag{26}$$

where $x \equiv \hbar\omega/\tau \equiv \hbar\omega/k_BT$ and

$$x_D \equiv \hbar\omega_D/k_BT \equiv \theta/T \ . \tag{27}$$

This defines the **Debye temperature** θ in terms of ω_D defined by (23). We may express θ as

$$\theta = \frac{\hbar v}{k_B} \cdot \left(\frac{6\pi^2 N}{V}\right)^{1/3} , \tag{28}$$

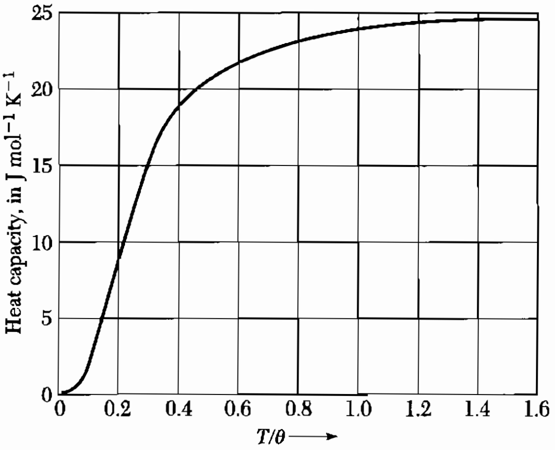


Figure 7 Heat capacity C_V of a solid, according to the Debye approximation. The vertical scale is in J mol^{-1} K^{-1}. The horizontal scale is the temperature normalized to the Debye temperature θ. The region of the T^3 law is below 0.1θ. The asymptotic value at high values of T/θ is 24.943 J mol^{-1} deg^{-1}.

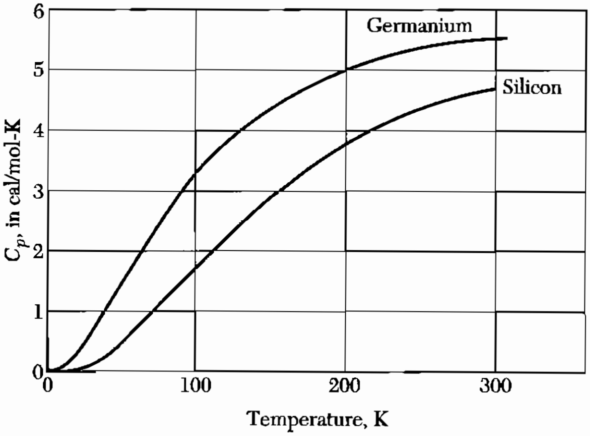


Figure 8 Heat capacity of silicon and germanium. Note the decrease at low temperatures. To convert a value in cal/mol-K to J/mol-K, multiply by 4.186.

so that the total phonon energy is

$$U = 9Nk_BT\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \, \frac{x^3}{e^x - 1} , \tag{29}$$

where N is the number of atoms in the specimen and $x_D = \theta/T$.

The heat capacity is found most easily by differentiating the middle expression of (26) with respect to temperature. Then

$$C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \, \frac{\omega^4 e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2} = 9Nk_B\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \, \frac{x^4 e^x}{(e^x - 1)^2} . \tag{30}$$

The Debye heat capacity is plotted in Fig. 7. At $T \gg \theta$ the heat capacity approaches the classical value of $3Nk_B$. Measured values for silicon and germanium are plotted in Fig. 8.

Debye T^3 Law

At very low temperatures we may approximate (29) by letting the upper limit go to infinity. We have

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \int_0^\infty dx\, x^3 \sum_{s=1}^\infty \exp(-sx) = 6 \sum_1^\infty \frac{1}{s^4} = \frac{\pi^4}{15} , \tag{31}$$

where the sum over s^{-4} is found in standard tables. Thus $U \cong 3\pi^4 N k_B T^4/5\theta^3$ for $T \ll \theta$, and

$$C_V \cong \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3 \cong 234\, N k_B \left(\frac{T}{\theta}\right)^3 , \tag{32}$$

which is the Debye T^3 approximation. Experimental results for argon are plotted in Fig. 9.

At sufficiently low temperature the T^3 approximation is quite good; that is, when only long wavelength acoustic modes are thermally excited. These are just the modes that may be treated as an elastic continuum with macroscopic elastic constants. The energy of the short wavelength modes (for which this approximation fails) is too high for them to be populated significantly at low temperatures.

We understand the T^3 result by a simple argument (Fig. 10). Only those lattice modes having $\hbar\omega < k_B T$ will be excited to any appreciable extent at a low temperature T. The excitation of these modes will be approximately classical, each with an energy close to $k_B T$, according to Fig. 1.

Of the allowed volume in **K** space, the fraction occupied by the excited modes is of the order of $(\omega_T/\omega_D)^3$ or $(K_T/K_D)^3$, where K_T is a "thermal" wavevector defined such that $\hbar v K_T = k_B T$ and K_D is the Debye cutoff wavevector. Thus the fraction occupied is $(T/\theta)^3$ of the total volume in **K** space. There are of the order of $3N(T/\theta)^3$excited modes, each having energy $k_B T$. The energy is $\sim 3Nk_B T(T/\theta)^3$, and the heat capacity is $\sim 12 N k_B (T/\theta)^3$.

For actual crystals the temperatures at which the T^3 approximation holds are quite low. It may be necessary to be below $T = \theta/50$ to get reasonably pure T^3 behavior.

Selected values of θ are given in Table 1. Note, for example, in the alkali metals that the heavier atoms have the lowest θ's, because the velocity of sound decreases as the density increases.

Einstein Model of the Density of States

Consider N oscillators of the same frequency ω_0 and in one dimension. The Einstein density of states is $D(\omega) = N\delta(\omega - \omega_0)$, where the delta function is centered at ω_0. The thermal energy of the system is

$$U = N\langle n \rangle \hbar\omega = \frac{N\hbar\omega}{e^{\hbar\omega/\tau} - 1} , \tag{33}$$

with ω now written in place of ω_0, for convenience.

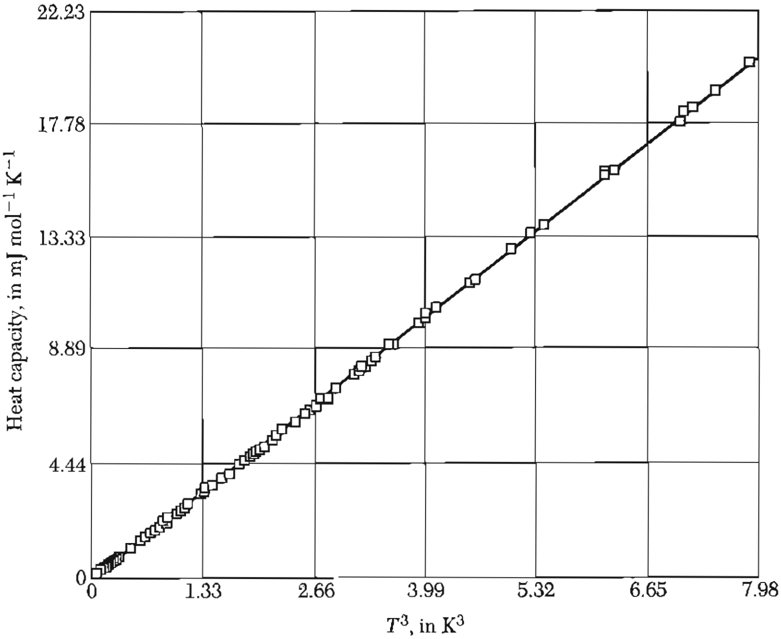


Figure 9 Low temperature heat capacity of solid argon, plotted against T^3. In this temperature region the experimental results are in excellent agreement with the Debye T^3 law with $\theta = 92.0$ K. (Courtesy of L. Finegold and N. E. Phillips.)

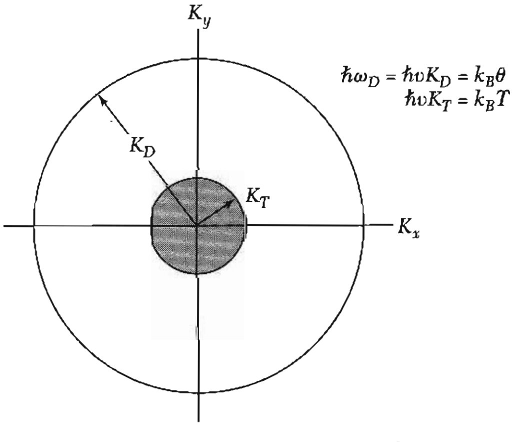


Figure 10 To obtain a qualitative explanation of the Debye T^3 law, we suppose that all phonon modes of wavevector less than K_T have the classical thermal energy k_BT and that modes between K_T and the Debye cutoff K_D are not excited at all. Of the $3N$ possible modes, the fraction excited is $(K_T/K_D)^3 = (T/\theta)^3$, because this is the ratio of the volume of the inner sphere to the outer sphere. The energy is $U \approx k_BT \cdot 3N(T/\theta)^3$, and the heat capacity is $C_V = \partial U/\partial T = 12Nk_B(T/\theta)^3$.

Table 1 Debye temperature and thermal conductivity

Low temperature limit of θ, in Kelvin

Thermal conductivity at 300 K, in W cm^{-1}K^{-1}

Li 344 0.85	Be 1440 2.00											B 0.27	C 2230 1.29	N	O	F	Ne 75
Na 158 1.41	Mg 400 1.56											Al 428 2.37	Si 645 1.48	P	S	Cl	Ar 92
K 91 1.02	Ca 230	Sc 360 0.16	Ti 420 0.22	V 380 0.31	Cr 630 0.94	Mn 410 0.08	Fe 470 0.80	Co 445 1.00	Ni 450 0.91	Cu 343 4.01	Zn 327 1.16	Ga 320 0.41	Ge 374 0.60	As 282 0.50	Se 90 0.02	Br	Kr 72
Rb 56 0.58	Sr 147	Y 280 0.17	Zr 291 0.23	Nb 275 0.54	Mo 450 1.38	Tc 0.51	Ru 600 1.17	Rh 480 1.50	Pd 274 0.72	Ag 225 4.29	Cd 209 0.97	In 108 0.82	Sn w 200 0.67	Sb 211 0.24	Te 153 0.02	I	Xe 64
Cs 38 0.36	Ba 110	La β 142 0.14	Hf 252 0.23	Ta 240 0.58	W 400 1.74	Re 430 0.48	Os 500 0.88	Ir 420 1.47	Pt 240 0.72	Au 165 3.17	Hg 71.9	Tl 78.5 0.46	Pb 105 0.35	Bi 119 0.08	Po	At	Rn
Fr	Ra	Ac															

Ce 0.11	Pr 0.12	Nd 0.16	Pm	Sm 0.13	Eu	Gd 200 0.11	Tb 0.11	Dy 210 0.11	Ho 0.16	Er 0.14	Tm 0.17	Yb 120 0.35	Lu 210 0.16
Th 163 0.54	Pa	U 207 0.28	Np 0.06	Pu 0.07	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

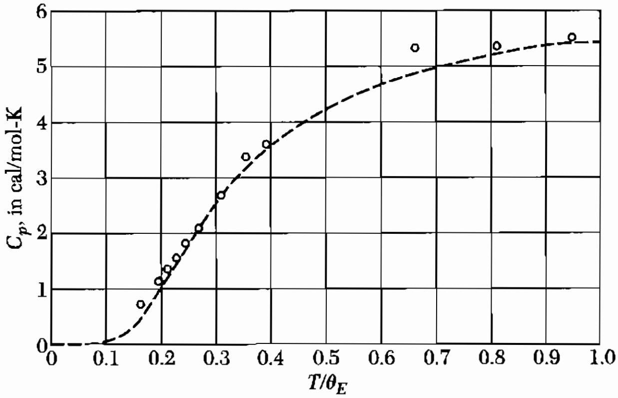


Figure 11 Comparison of experimental values of the heat capacity of diamond with values calculated on the earliest quantum (Einstein) model, using the characteristic temperature $\theta_E = \hbar\omega/k_B = 1320$ K. To convert to J/mol-deg, multiply by 4.186.

The heat capacity of the oscillators is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = Nk_B\left(\frac{\hbar\omega}{\tau}\right)^2\frac{e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau}-1)^2} , \tag{34}$$

as plotted in Fig. 11. This expresses the Einstein (1907) result for the contribution of N identical oscillators to the heat capacity of a solid. In three dimensions N is replaced by $3N$, there being three modes per oscillator. The high temperature limit of C_V becomes $3Nk_B$, which is known as the Dulong and Petit value.

At low temperatures (34) decreases as $\exp(-\hbar\omega/\tau)$, whereas the experimental form of the phonon contribution is known to be T^3as accounted for by the Debye model treated above. The Einstein model, however, is often used to approximate the optical phonon part of the phonon spectrum.

General Result for D(ω)

We want to find a general expression for $D(\omega)$, the number of states per unit frequency range, given the phonon dispersion relation $\omega(\mathbf{K})$. The number of allowed values of $\mathbf{K}$ for which the phonon frequency is between ω and $\omega + d\omega$ is

$$D(\omega)\,d\omega = \left(\frac{L}{2\pi}\right)^3\int_{\text{shell}} d^3K , \tag{35}$$

where the integral is extended over the volume of the shell in $\mathbf{K}$ space bounded by the two surfaces on which the phonon frequency is constant, one surface on which the frequency is ω and the other on which the frequency is $\omega + d\omega$.

The real problem is to evaluate the volume of this shell. We let dS_ω denote an element of area (Fig. 12) on the surface in $\mathbf{K}$ space of the selected constant

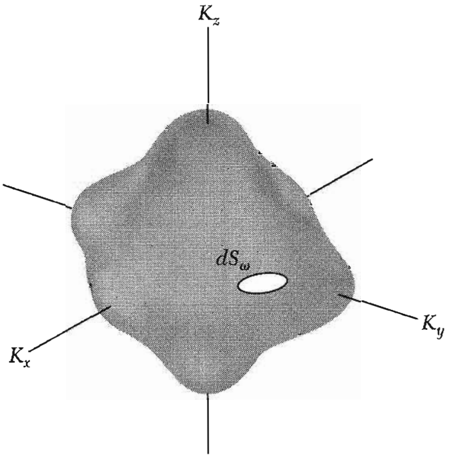


Figure 12 Element of area dS_ω on a constant frequency surface in **K** space. The volume between two surfaces of constant frequency at ω and $\omega + d\omega$ is equal to $\int dS_\omega \, d\omega / |\nabla_{\mathbf{K}}\omega|$.

frequency ω. The element of volume between the constant frequency surfaces ω and $\omega + d\omega$ is a right cylinder of base dS_ω and altitude $dK_\perp$, so that

$$\int_{\text{shell}} d^3K = \int dS_\omega dK_\perp \ , \tag{36}$$

Here $dK_\perp$ is the perpendicular distance (Fig. 13) between the surface ω constant and the surface $\omega + d\omega$ constant. The value of $dK_\perp$ will vary from one point to another on the surface.

The gradient of ω, which is $\nabla_{\mathbf{K}}\omega$, is also normal to the surface ω constant, and the quantity

$$|\nabla_{\mathbf{K}}\omega| \, dK_\perp = d\omega \ ,$$

is the difference in frequency between the two surfaces connected by $dK_\perp$. Thus the element of the volume is

$$dS_\omega \, dK_\perp = dS_\omega \frac{d\omega}{|\nabla_{\mathbf{K}}\omega|} = dS_\omega \frac{d\omega}{v_g} \ ,$$

where $v_g = |\nabla_{\mathbf{K}}\omega|$ is the magnitude of the group velocity of a phonon. For (35) we have

$$D(\omega) \, d\omega = \left(\frac{L}{2\pi}\right)^3 \int \frac{dS_\omega}{v_g} d\omega \ .$$

We divide both sides by $d\omega$ and write $V = L^3$ for the volume of the crystal: the result for the density of states is

$$\boxed{D(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{v_g} \ .} \tag{37}$$

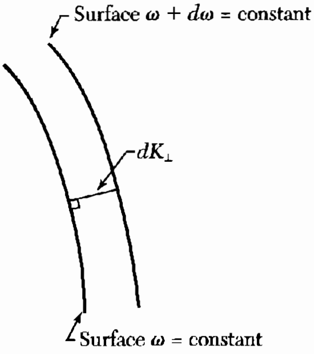
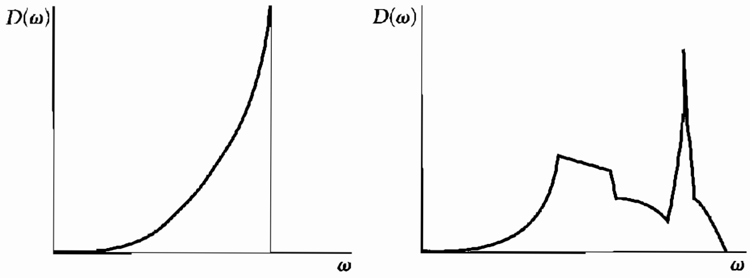


Figure 13 The quantity $dK_\perp$ is the perpendicular distance between two constant frequency surfaces in **K** space, one at frequency ω and the other at frequency $\omega + d\omega$.



(a)

(b)

Figure 14 Density of states as a function of frequency for (a) the Debye solid and (b) an actual crystal structure. The spectrum for the crystal starts as ω^2 for small ω, but discontinuities develop at singular points.

The integral is taken over the area of the surface ω constant, in **K** space. The result refers to a single branch of the dispersion relation. We can use this result also in electron band theory.

There is a special interest in the contribution to $D(\omega)$ from points at which the group velocity is zero. Such critical points produce singularities (known as Van Hove singularities) in the distribution function (Fig. 14).

ANHARMONIC CRYSTAL INTERACTIONS

The theory of lattice vibrations discussed thus far has been limited in the potential energy to terms quadratic in the interatomic displacements. This is the harmonic theory; among its consequences are:

- Two lattice waves do not interact; a single wave does not decay or change form with time.
- There is no thermal expansion.
- Adiabatic and isothermal elastic constants are equal.
- The elastic constants are independent of pressure and temperature.
- The heat capacity becomes constant at high temperatures $T > \theta$.