

MAIN PROGRAM

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37 CONTINUE
  IF(EP<1>.GT.EP<2>).OR.EP<2>.GT.EP<3>).OR.EP<3>.GT.EP<4>).
  1 OR.EP<4>.GT.EP<5>)GOTO 39
C THE PROGRAM NOW STARTS TO SEARCH FOR VALUES OF ENERGY SUCH THAT
C THE WAVE FUNCTION VANISHES AT L3.
C IN THE FIRST PART OF THE SEARCH FOR THE N'TH EIGENSTATE BY
C USING A BISECTION TECHNIQUE THE PPROGRAM FINDS TWO ENERGIES, ONE ABOVE
C AND ONE BELOW THE TRUE N'TH ENERGY LEVEL, WHERE THE NUMBER OF NODES
C ARE N-1 AND N RESPECTIVELY. THESE ENERGIES ARE THEN USED AS STARTING
C POINTS FOR THE LINEAR INTERPOLATION ROOT FINDING FUNCTION.
  EF=AMINI(0.0,UP)
  CALL PL3FEN(EF,PL3F,NODES)
  DO 38 N=1,4
    ET=(EP(N)+EP(N+1))*0.5
    GAP=ABS(ET-EF)
    IF(GAP.EQ.0.0)GAP=EUK(1)
    ET=EF+GAP
    BOOL=.FALSE.
    DO 40 J=1,500
      CALL PL3FEN(ET,PL3T,NODES)
      PL3S=PL3T
      IF(NODES.GT.N)GOTO 76
      IF(NODES.LT.N)GOTO 78
      ES=ET
      GOTO 44
76 CONTINUE
      BOOL=.TRUE.
      ET=ET-GAP
      GOTO 42
78 CONTINUE
      ET=ET+GAP
42 CONTINUE
      IF(BOOL)GAP=GAP*0.5
      IF(.NOT.BOOL)GAP=GAP*2.0
40 CONTINUE
      WRITE(1,214)N
214 FORMAT(1H0,49H WARNING - THE PROGRAM FAILED TO FIND A CORRECT ,
1 9HSTARTING ,/,26HPOINT FOR THE SEARCH WITH ,I4,6H NODES)
      ES=ET
44 CONTINUE
C THE ACCURACY FOUND BY EFPL30 IS SET BY THE PARAMETERS EAC AND FAC.
      EAC=EUK(1)*1.0E-5
      FAC=1.0E-5
      E(I,N)=EFPL30(EF,ES,PL3F,PL3S,EAC,FAC)
      IF(N-4)45,38,38
45 CONTINUE
      EF=ET
      PL3F=PL3T
38 CONTINUE
      WRITE(1,130)UP,E(I,1),E(I,2),E(I,3),E(I,4)
130 FORMAT(1H ,5(E11.4,3X))
34 CONTINUE
C THE OPTION IS NOW PROVIDED OF PLOTTING A GRAPH OF E AGAINST UP ON THE
C PRINTER.
C
C
C

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MAIN PROGRAM

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C   THE OPTION IS PROVIDED OF PLOTTING A GRAPH ON THE LINE PRINTER.
C   IF YES OR NO IS ENTERED AS REQUIRED IT CAN BE READ IN A
C   FORMAT AND COMPARED WITH THE VARIABLES Y(=4HYES ,) AND
C   YN(=4HNO ,) SET IN THE DATA STATEMENT. IF A GRAPH IS NOT REQUIRED
C   CONTROL CAN BE TRANSFERED TO STATEMENT 62
C
      WRITE(1,208)
      WRITE(1,170)
170  FORMAT(//44HDO YOU WANT TO PLOT OUT THESE RESULTS AS AN,
      1 17HAPPROXIMATE GRAPH,/35H ON THE TELETYPE. TYPE YES OR NO.)
      64 CONTINUE
      READ(1,171)YON
171  FORMAT(A4)
      IF(YON.EQ.Y)GOTO 60
      IF(YON.EQ.YN)GOTO 62
      WRITE(1,174)
174  FORMAT(1H ,40HRESPONSE NOT RECOGNISED. TYPE YES OR NO)
      GOTO 64
      60 CONTINUE
*****
C   THE MAXIMUM WIDTH OF THE GRAPH IS SET BY THE PARAMETER IWG. THIS
C   IS CHOSEN SUCH THAT IWG-1 IS A MULTIPLE OF NUP-1
      IWG=70
      GAP=FLOAT(IWG-1)/FLOAT(NUP-1)
      IGAP=IFIX(AINT(GAP))
      IWG=(NUP-1)*IGAP+1
      DDUP=ABS(DUP/FLOAT(IGAP))
C   FIND THE MAXIMUM AND MINIMUM VALUES OF THE ENERGY
      EMIN=E(1,1)
      EMAX=E(1,1)
      DO 66 N=1,4
      DO 68 I=2,NUP
      IF(E(I,N).LT.EMIN)EMIN=E(I,N)
      IF(E(I,N).GT.EMAX)EMAX=E(I,N)
68  CONTINUE
66  CONTINUE
      IF(EMIN.GT.0.0)EMIN=0.0
C   THE HEIGHT OF THE GRAPH IS SET BY THE PARAMETER IHG
      IHG=IWG
      SCALE=(EMAX-EMIN)/FLOAT(IHG-1)
C   WRITE OUT HEADING FOR THE GRAPH
      UP2=UP1+FLOAT(NUP-1)*DDUP
      WRITE(1,208)
      WRITE(1,218)
218  FORMAT(1H ,48HAPPROXIMATE GRAPH OF THE ENERGIES OF THE GROUND ,
      1 21HSTATE AND FIRST THREE)
      WRITE(1,220)
220  FORMAT(1H ,49HEXCITED STATES AS A FUNCTION OF THE PERTURBATION ,
      1 20HUP. UP IS PLOTTED ON)
      WRITE(1,222)UP1,UP2
222  FORMAT(1H ,36HTHE HORIZONTAL AXIS AND VARIES FROM ,E11.4,4H TO ,
      1 E11.4)
      WRITE(1,224)EMAX
224  FORMAT(1H ,47HTHE ENERGY IS PLOTTED ON THE VERTICAL AXIS AND ,
      1 12HVARIES FROM ,E11.4)
      WRITE(1,226)EMIN

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MAIN PROGRAM

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226 FORMAT(1H ,10X,3HTO ,E11.4)
WRITE(1,208)
C PLOT GRAPH
DO 70 J=1,IHG
ETS=EMAX-SCALE*(FLOAT(J)-1.5)
EBS=EMAX-SCALE*(FLOAT(J)-0.5)
DO 72 I=1,NUP
K1=(I-1)*IGAP+1
K2=I*IGAP
DO 74 K=K1,K2
PLOT(K)=PLOTS
IF(ETS.GE.0.0.AND.EBS.LT.0.0)PLOT(K)=PLOT6
UP=UP1+DUP*(FLOAT(K-1)/FLOAT(IGAP))
IF(UP.LE.(DDUP/2.0).AND.UP.GT.(-DDUP/2.0))PLOT(K)=PLOT7
74 CONTINUE
IF(E(I,1).LE.ETS.AND.E(I,1).GT.EBS)PLOT(K1)=PLOT1
IF(E(I,2).LE.ETS.AND.E(I,2).GT.EBS)PLOT(K1)=PLOT2
IF(E(I,3).LE.ETS.AND.E(I,3).GT.EBS)PLOT(K1)=PLOT3
IF(E(I,4).LE.ETS.AND.E(I,4).GT.EBS)PLOT(K1)=PLOT4
72 CONTINUE
WRITE(1,178)(PLOT(K),K=1,IHG)
178 FORMAT(1H ,120A1)
70 CONTINUE
62 CONTINUE
C
C THE OPTION IS NOW PROVIDED - WITH AN INTERACTIVE SYSTEM - OF TRYING
C DIFFERENT SETS OF UP'S.
C
WRITE(1,132)
132 FORMAT(/54HDO YOU WANT TO RE-RUN THE PROGRAM WITH THE SAME VALUES,
1 14HFOR L1, L2, L3,/41HAND MP BUT WITH DIFFERENT VALUES FOR THE ,
2 24HPERTURBING POTENTIAL UP.,/15H TYPE YES OR NO)
46 CONTINUE
READ(1,171)YON
IF(YON.EQ.Y)GOTO 28
IF(YON.EQ.YN)GOTO 48
WRITE(1,136)
136 FORMAT(39HRESPONSE NOT RECOGNISED. TYPE YES OR NO)
GOTO 46
48 CONTINUE
C
C OUTPUT SUPPLEMENTARY INFORMATION TO AID STUDENT'S PERTURBATION
C CALCULATION.
WRITE(1,208)
WRITE(1,228)
228 FORMAT(1H ,5X,1HN,6X,15HSIN(N*PI*L1/L3),6X,15HSIN(N*PI*L2/L3))
WRITE(1,208)
WRITE(1,140)(I,SL1(I),SL2(I),I=1,14)
140 FORMAT(4X,I2,8X,F10.6,11X,F10.6)
WRITE(1,312)
312 FORMAT(1H ,16HPROGRAM FINISHED)
STOP
END

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SUBROUTINE PL3FE

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      SUBROUTINE PL3FEN(E,PL3FE,NODES)
C  SUBROUTINE TO RETURN THE VALUE OF THE WAVE FUNCTION AT L3
C  AND THE NUMBER OF NODES BETWEEN 0 AND L3
C  GIVEN THE ENERGY E, THE PERTURBATION UP AND THE DIMENSIONS.
C  THE DIMENSIONS (=L1,L2,L3), PERTURBING POTENTIAL (=UP) AND
C  PARTICLE MASS (=MP) ARE ALL TRANSFERED IN THE COMMON BLOCK.
C  THE MNEMONICS USED FOR THESE ARE AS IN THE MAIN PROGRAM.
      COMMON L1,L2,L3,UP,MP,N,PI
      REAL L1,L2,L3,MP,K1,K2
C  IF UP = 0 THE CALCULATION OF THE WAVE FUNCTION AT
C  L3 IS SIMPLE.
      IF(UP.NE.0.0)GOTO 1
      IF(E)S,7,3
      7 CONTINUE
      PL3FE=L3
      NODES=0
      GOTO 24
      3 CONTINUE
      K1=SQRT(MP*E)
      PL3FE=SIN(K1*L3)/K1
      NODES=IFIX(L3*K1/PI)
      GOTO 24
      5 CONTINUE
      NODES=0
      ALPHA=SQRT(-MP*E)
      F1=EXP(ALPHA*L3)
      F2=1.0/F1
      PL3FE=(F1-F2)/(2.0*ALPHA)
      GOTO 24
      1 CONTINUE
      NODES=0
C  CALCULATE THE WAVE FUNCTION AT L1 (=PL1) AND ITS SLOPE AT L1 (=DPL1)
      IF(E)2,4,6
      2 CONTINUE
      ALPHA=SQRT(-MP*E)
      F1=EXP(ALPHA*L1)
      F2=1.0/F1
      PL1=(F1-F2)/(2.0*ALPHA)
      DPL1=(F1+F2)/2.0
      GOTO 8
      4 CONTINUE
      PL1=L1
      DPL1=1.0
      GOTO 8
      6 CONTINUE
      K1=SQRT(MP*E)
      PL1=SIN(K1*L1)/K1
      DPL1=COS(K1*L1)
      NODES=IFIX(L1*K1/PI)
      8 CONTINUE
C  CALCULATE THE WAVE FUNCTION AT L2 (=PL2) AND ITS SLOPE AT L2 (=DPL2)
      IF(E-UP)10,12,14
      10 CONTINUE
      BETA=SQRT(-MP*(E-UP))
      F1=EXP(BETA*(L1-L2))
      A=PL1-DPL1/BETA

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SUBROUTINE PL3FE

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      B=PL1+DPL1/BETA
      PL2=A*F1/2.0+B/(2.0*F1)
      DPL2=BETA*(-A*F1/2.0+B/(2.0*F1))
      IF(PL1.EQ.0.0)GOTO 16
      IF(PL2.NE.0.0)GOTO 11
      NODES=NODES+1
      GOTO 16
11  CONTINUE
      IF((PL1/PL2).LT.0.0)NODES=NODES+1
      GOTO 16
12  CONTINUE
      A=DPL1
      B=PL1-A*L1
      PL2=A*L2+B
      DPL2=A
      IF(PL1.EQ.0.0)GOTO 16
      IF(PL2.NE.0.0)GOTO 13
      NODES=NODES+1
      GOTO 16
13  CONTINUE
      IF((PL1/PL2).LT.0.0)NODES=NODES+1
      GOTO 16
14  CONTINUE
      K2=SQRT(MP*(E-UP))
      IF(L1.NE.0.0)GOTO 15
      PL2=SIN(K2*L2)/K2
      DPL2=COS(K2*L2)
      NODES=NODES+IFIX(L2*K2/PI)
      GOTO 16
15  CONTINUE
      DELTA=ATAN(K2*PL1/DPL1)-K2*L1
      A=PL1/SIN(K2*L1+DELTA)
      PL2=A*SIN(K2*L2+DELTA)
      DPL2=K2*A*COS(K2*L2+DELTA)
      NODES=NODES+IFIX((L2*K2+DELTA)/PI+1.0)-IFIX((L1*K2+DELTA)/PI+1.0)
16  CONTINUE
C  CALCULATE THE WAVE FUNCTION AT L3 (=PL3FE)
      IF(E>18,20,22)
18  CONTINUE
      F1=EXP(ALPHA*L2)
      B=(PL2+DPL2/ALPHA)/(2.0*F1)
      A=PL2*F1-B*F1*F1
      F1=EXP(ALPHA*L3)
      PL3FE=A/F1+B*F1
      IF(PL2.EQ.0.0)GOTO 24
      IF(PL3FE.NE.0.0)GOTO 17
      NODES=NODES+1
      GOTO 24
17  CONTINUE
      IF((PL2/PL3FE).LT.0.0)NODES=NODES+1
      GOTO 24
20  CONTINUE
      A=DPL2
      B=PL2-A*L2
      PL3FE=A*L3+B
      IF(PL2.EQ.0.0)GOTO 24

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SUBROUTINE PL3FE

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      IF<PL3FE.NE.0.0>GOTO 19
      NODES=NODES+1
      GOTO 24
19  CONTINUE
      IF<(PL2/PL3FE).LT.0.0>NODES=NODES+1
      GOTO 24
22  CONTINUE
      IF<L2.NE.L3>GOTO 26
      PL3FE=PL2
      GOTO 24
26  CONTINUE
      DELTA=ATAN(K1*PL2/DPL2)-K1*L2
      A=PL2/SIN(K1*L2+DELTA)
      PL3FE=A*SIN(K1*L3+DELTA)
      NODES=NODES+IFIX<(L3*K1+DELTA)/PI+1.0>-IFIX<(L2*K1+DELTA)/PI+1.0>
24  CONTINUE
      RETURN
      END

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FUNCTION EFPL30

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      FUNCTION EFPL30(EF,ES,PL3F,PL3S,EAC,FAC)
C   THIS FUNCTION LOCATES THE VALUE OF THE ENERGY =EFPL30 WHEN THE WAVE
C   FUNCTION AT L3 IS ZERO IN THE INTERVAL EF TO ES BY A COMBINATION OF
C   THE METHODS OF LINEAR EXTRAPOLATION, INTERPOLATION AND BISECTION.
C   THE ACCURACY IS SPECIFIED BY THE PARAMETERS EAC AND FAC.
      COMMON L1,L2,L3,UP,MP,N,PI
      REAL L1,L2,L3,MP
      LOGICAL SWITCH
      SWITCH=.FALSE.
      EA=EF
      EB=ES
      PL3A=PL3F
      PL3B=PL3S
      EX=PL3S*(ES-EF)/(PL3S-PL3F)
      ET=ES-EX
      DO 2 I=1,1000
      CALL PL3FEN(ET,PL3T,NODES)
      IF(ABS(PL3T).GT.(L3*FAC))GOTO 16
      EFPL30=ET
      GOTO 14
16  CONTINUE
C   TEST IF ET LIES OUTSIDE PREVIOUSLY FOUND VALUES
      IF(ET.GE.EB.OR.ET.LE.EA)GOTO 4
C   TEST WHETHER EXTRAPOLATION WOULD INVOLVE DIVISION BY 0
      IF(PL3T.EQ.PL3S)GOTO 4
C   RESET EA AND EB
      IF(NODES.EQ.N)GOTO 10
      EA=ET
      PL3A=PL3T
      GOTO 12
10  CONTINUE
      EB=ET
      PL3B=PL3T
12  CONTINUE
C   USE LINEAR EXTRAPOLATION
      EF=ES
      PL3F=PL3S
      ES=ET
      PL3S=PL3T
      EX=PL3S*(ES-EF)/(PL3S-PL3F)
      IF((ABS(EX)).LT.EAC)GOTO 6
      IF(ET.EQ.0.0)GOTO 18
      IF(ABS(EX/ET).LT.FAC)GOTO 6
18  CONTINUE
      ET=ES-EX
      GOTO 2
4   CONTINUE
      IF(SWITCH)GOTO 8
C   USE LINEAR INTERPOLATION FROM THE TWO CLOSEST PREVIOUS VALUES
      EX=PL3A*(EA-EB)/(PL3A-PL3B)
      ET=EA-EX
      SWITCH=.TRUE.
      IF(ABS(EX).GT.EAC)GOTO 2
      IF(ET.EQ.0.0)GOTO 2
      IF(ABS(EX/ET).GT.FAC)GOTO 2
20  CONTINUE

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FUNCTION EFPL30

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      EFPL30=ET
      GOTO 14
    8 CONTINUE
C  ALTERNATIVELY, USE BISECTION FROM TWO CLOSEST PREVIOUS VALUES
      EX=(EA-EB)*0.5
      ET=(EA+EB)*0.5
      SWITCH=.FALSE.
      IF(ABS(EX).GT.EAC)GOTO 2
      IF(ET.EQ.0.0)GOTO 22
      IF(ABS(EX/ET).LT.FAC)GOTO 6
    22 CONTINUE
      EFPL30=ET
      GOTO 14
    2 CONTINUE
      WRITE(1,100)N
100  FORMAT(1H ,44HWARNING : PROGRAM DOES NOT FIND THE CORRECT ,11,
1    3H TH)
      WRITE(1,102)UP
102  FORMAT(1H ,20HEIGENSTATE FOR UP = ,E12.5)
      EFPL30=ES
      GOTO 14
    6 CONTINUE
      EFPL30=ES-EX
14  CONTINUE
      RETURN
      END

```


CHAPTER 9

Simulation of Phonon Dispersion Curves and Density of States

G. J. KEELER

1. INTRODUCTION

In order to study the vibrational properties of crystalline solids, it is necessary to know in detail the frequency dependence of the normal modes of vibration of the crystal lattice.

Neutron-scattering measurements and other experimental observations provide overwhelming evidence that the normal modes are quantized, with energy $\hbar\omega$, and these quantized vibrations are referred to as phonons. An understanding of both the microscopic properties of the phonons, and macroscopic properties related to thermal vibrations (such as the specific heat and optical properties of insulating materials), requires a knowledge of the phonon dispersion curves and density of states.

In spite of the fundamental role played by the density states, it is very difficult to measure directly, and is almost invariably computed. Experimental data will normally give information on the phonon dispersion curves, and these will then be used to determine the interatomic force constants, by comparing the experimental curves with those calculated from the force constants. Even when these have been determined, it is by no means simple to calculate the density of states analytically, but modern computing methods have proved an ideal tool for solving the problem numerically.

2. LINEAR ATOMIC CHAIN

2.1 Dispersion curves

Before discussing dispersion curves in detail, it is worth pointing out that although calculation of specific heats, for example, requires a quantum-mechanical treatment, phonon dispersion curves can be calculated from a purely classical treatment.

Many of the salient features of lattice vibrations can be most clearly illustrated by consideration of a linear chain of atoms, as shown in Figure 1.

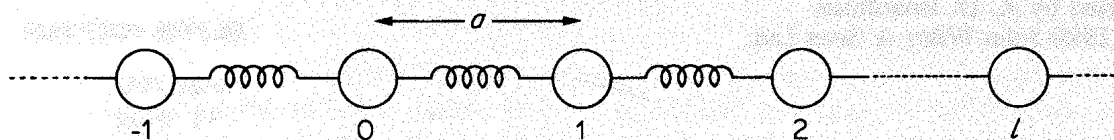


Figure 1. Linear chain of identical atoms, shown schematically with interatomic forces between nearest neighbours only.

We suppose that there are interactions between each pair of atoms in the chain (although Figure 1 has for simplicity been drawn to suggest forces between nearest neighbours only). We shall assume that the forces obey Hooke's law, i.e. they are linear in the relative displacements of the atoms (the 'harmonic approximation'), and we can then define interatomic force constants γ_l such that if u_l denotes the displacement of the l th atom, then the force on the atom at the origin due to the displacement u_l is

$$F_0 = +\gamma_l(u_l - u_0). \quad (1)$$

Summing over all atoms (l +ve and -ve), the equation of motion of the atom at the origin is

$$m \frac{\partial^2 u_0}{\partial t^2} = \sum_{l \neq 0} \gamma_l(u_l - u_0). \quad (2)$$

If we look for a solution for u_0 in the form of a wave of frequency ω and wave number $k (= 2\pi/\lambda)$ travelling in the x -direction, this will have the general form

$$u(x) = A e^{i(\omega t - kx)}. \quad (3)$$

However, we need only consider displacements at actual atomic sites, so if the lattice spacing is a ,

$$u_l = A e^{i(\omega t - kla)},$$

giving

$$-m\omega^2 A e^{i\omega t} = \sum_{l \neq 0} \gamma_l A \{e^{i(\omega t - kla)} - e^{i\omega t}\}. \quad (4)$$

Since by symmetry $\gamma_l = \gamma_{-l}$, we may rewrite this, after cancellation, as

$$m\omega^2 = \sum_{l>0} 2\gamma_l(1 - \cos kla). \quad (5)$$

Consider the simple example of nearest-neighbour interactions only ($\gamma_1 = \gamma$, $\gamma_2 = \gamma_3 = \dots = 0$). Then equation (5) gives

$$\omega^2(k) = \frac{2\gamma}{m}(1 - \cos ka), \quad \text{or} \quad \omega(k) = 2\sqrt{\frac{\gamma}{m}} |\sin \frac{1}{2}ka|. \quad (6)$$

Thus the ω - k relationship, which we call the *dispersion curve*, is periodic in k as shown in Figure 2. However, let us consider the physical significance of this periodicity by looking at the relative motion of two successive atoms:

$$\frac{u_1}{u_0} = \frac{Ae^{i(\omega t - ka)}}{Ae^{i\omega t}} = e^{-ika}. \quad (7)$$

Thus a range of values of k of $2\pi/a$ covers all possible values of u_1/u_0 . Since k must be allowed both positive and negative values to represent waves propagating in either direction, the range of independent values of k is

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}, \quad (8)$$

and this is called the *first Brillouin zone*.

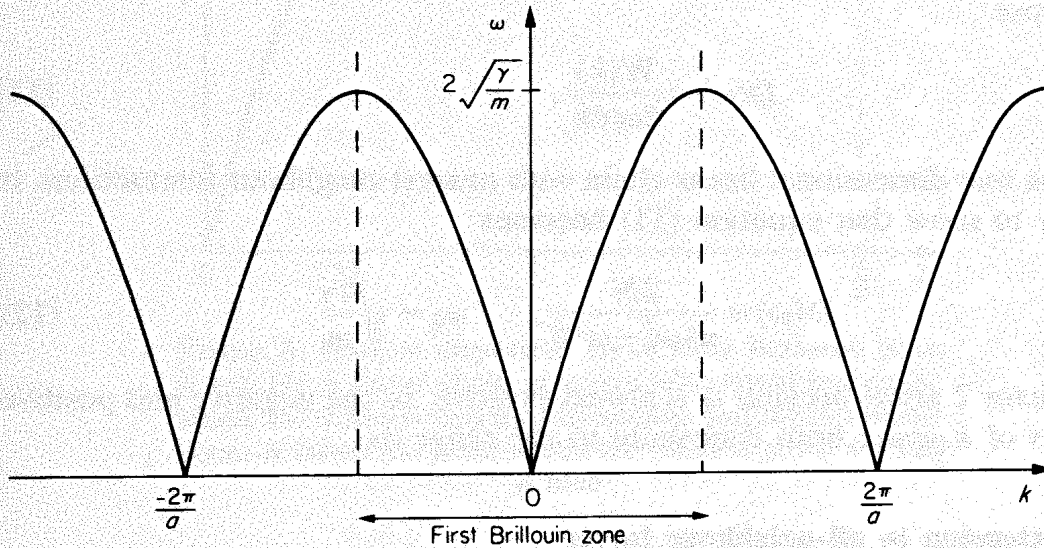


Figure 2. Plot of ω versus k (phonon dispersion curve) for a linear chain of atoms with interactions between nearest neighbours only.

2.2 Density of states

The above treatment assumes that all values of k are possible. However, physically the chain must be bounded, so that we must apply appropriate boundary conditions. The particular choice of boundary condition affects only the fine details of the density of states, and it is sufficient to consider the most commonly utilized boundary condition, which is for the solution to be periodic over a very large number of lattice spacings, N . Thus $u_l = u_{l+N}$, i.e.

$$e^{-ikla} = e^{-ik(l+N)a} \quad \text{or} \quad e^{-ikNa} = 1.$$

Hence, $kNa = 2n\pi$, where n is any integer, or

$$k = 0, \pm \frac{2\pi}{aN}, \pm \frac{2\pi}{a} \frac{2}{N}, \dots, \pm \frac{2\pi}{a} \frac{\frac{1}{2}N}{N}, \quad (9)$$

i.e. there are approximately N possible values of k , evenly distributed throughout k -space with an interval $2\pi/Na$. Thus the *density of states in k -space*, $W(k)$ —that is, the number of possible modes of vibration per unit interval in k —is a constant given by $2\pi W(k)/Na = 1$ or $W(k) = Na/2\pi$.

Of more interest, however, is the density of states as a function of frequency, $D(\omega)$. Now the number of states in a small frequency interval $d\omega$ will be

$$D(\omega) d\omega = W(k) dk = W(k) \frac{dk}{d\omega} d\omega; \quad (10)$$

therefore

$$D(\omega) = \frac{W(k)}{d\omega/dk}. \quad (11)$$

For the one-dimensional linear chain with nearest-neighbour interactions, it is easy to show that equation (11) becomes

$$D(\omega) = \frac{2N}{\pi(\omega_0^2 - \omega^2)^{\frac{1}{2}}}, \quad \omega_0 = \sqrt{\frac{4\gamma}{m}}. \quad (12)$$

The factor 2 arises because ω is always positive, so the negative and positive regions of k -space both contribute to the range $d\omega$.

2.3 Extension to all-neighbour forces

The simple form of dispersion curve shown in Figure 2 is a result of assuming nearest-neighbour forces only. Extension to further neighbours is quite simple in one dimension. For instance, if $\gamma_1 \neq 0$ and $\gamma_2 \neq 0$, equation (5) gives

$$\omega^2 = \frac{2}{m} (\gamma_1 + \gamma_2 - \gamma_1 \cos ka - \gamma_2 \cos 2ka). \quad (13)$$

Figure 3 illustrates the case $\gamma_1 = \gamma_2$.

2.4 More than one atom per unit cell

Considerable complication occurs when the atoms in the chain are not all equivalent. Variations may occur in the masses, the force constants, and the atomic spacing. However, the essential features can be illustrated if we

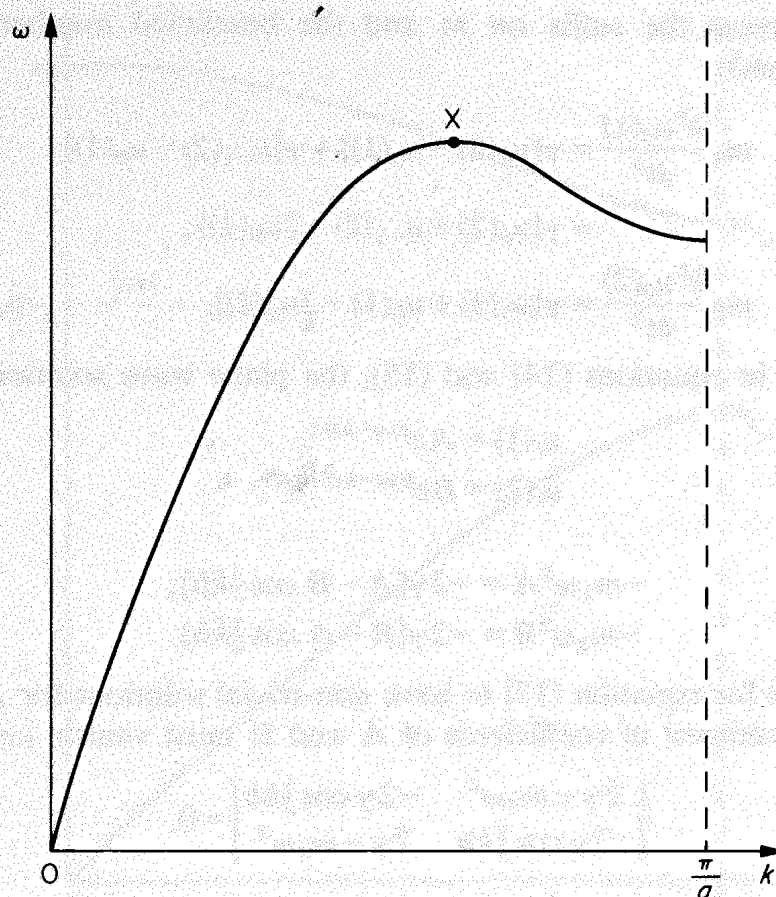


Figure 3. Phonon dispersion curve (first Brillouin zone, $k > 0$) for a linear chain of atoms with equal force constants for nearest- and second-nearest-neighbour interactions. X labels the point where the phonon group velocity is zero

assume even atomic spacing, a single, nearest-neighbour force constant γ , but different atomic masses, as shown in Figure 4.

The lattice spacing b is now the distance between like atoms (i.e. $b = 2a$), since the *unit cell* now contains two atoms. Thus we have two equations of motion, for the two types of atom (note that the suffix on u labels atom

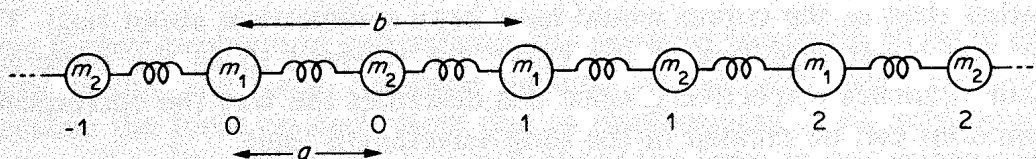


Figure 4. Linear chain of atoms of two species, having different masses but identical spacing and force constants. Although the distance apart is still a , the unit cell is of size $b = 2a$.

position, whereas the suffix on m and the bracketed number label the species of atom):

$$\begin{aligned} m_1 \frac{\partial^2 u_0(1)}{\partial t^2} &= \gamma \{u_0(2) - u_0(1)\} + \gamma \{u_{-1}(2) - u_0(1)\} \\ &= \gamma \{u_0(2) + u_{-1}(2) - 2u_0(1)\}; \end{aligned} \quad (14)$$

$$m_2 \frac{\partial^2 u_0(2)}{\partial t^2} = \gamma \{u_1(1) + u_0(1) - 2u_0(2)\}. \quad (15)$$

We now use, in equations (14) and (15), the plane wave solution

$$\begin{aligned} u_1(1) &= A e^{i(\omega t - k l b)}, \\ u_1(2) &= B e^{i[\omega t - k(l + \frac{1}{2}b)]}. \end{aligned} \quad (16)$$

This gives

$$\begin{aligned} -m_1 \omega^2 A &= -2\gamma \{A - B \cos \tfrac{1}{2}kb\}; \\ -m_2 \omega^2 B &= -2\gamma \{B - A \cos \tfrac{1}{2}kb\}. \end{aligned} \quad (17)$$

The condition for equation (17) to have non-trivial solutions for A and B is that the determinant of coefficients of A and B must vanish, i.e.

$$\begin{vmatrix} 2\gamma - m_1 \omega^2 & -2\gamma \cos \tfrac{1}{2}kb \\ -2\gamma \cos \tfrac{1}{2}kb & 2\gamma - m_2 \omega^2 \end{vmatrix} = 0, \quad (18)$$

giving

$$\omega^2 = \gamma \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \pm \gamma \left[\left(\frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4 \sin^2 \tfrac{1}{2}kb}{m_1 m_2} \right]^{\frac{1}{2}}. \quad (19)$$

We can write this as

$$\omega^2 = \tfrac{1}{2} \omega_0^2 [1 \pm \sqrt{1 - C \sin^2 \tfrac{1}{2}kb}] \quad (20)$$

where $\omega_0^2 = 2\gamma(1/m_1 + 1/m_2)$ and C is commonly called a coupling coefficient, defined as

$$C = \frac{4m_1 m_2}{(m_1 + m_2)^2} = \frac{4\rho}{(1 + \rho)^2}, \quad \rho = \frac{m_1}{m_2}. \quad (21)$$

The dispersion curve is now as shown in Figure 5 (note that had we plotted ω^2 rather than ω , the curves would have been symmetrical about $\tfrac{1}{2}\omega_0^2$). The upper and lower branches of the curve are referred to as the optic and acoustic branches respectively, since this describes the way the corresponding phonons can be created in the long-wavelength limit.

We would expect that as $m_1 \rightarrow m_2$, the above case should go over smoothly to the single atom case, and a quick check of equation (19) above will confirm this, but the dispersion curve would appear to be quite different. However, the anomaly is resolved if we remember that $b = 2a$, and when

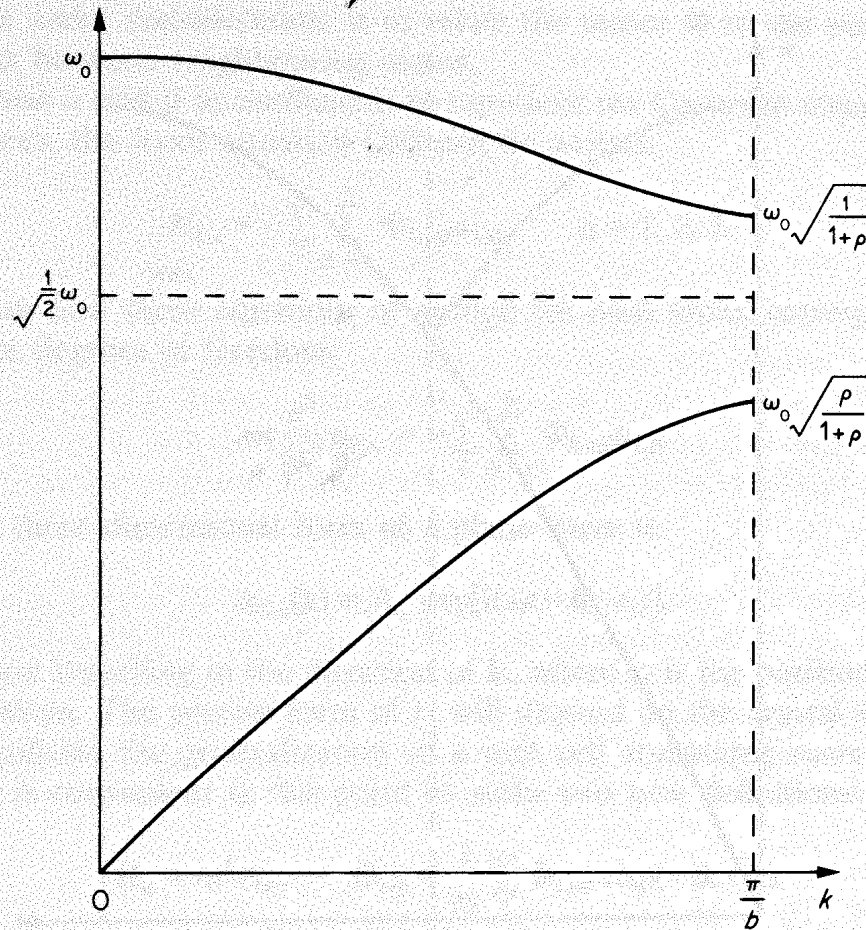


Figure 5. Phonon dispersion curve for a diatomic linear chain, with atoms of different masses m_1 and m_2 (where $\rho = m_1/m_2$, m_1 being the smaller mass) but identical spacing and force constants (between nearest neighbours only)

$m_1 \neq m_2$, the Brillouin zone is halved in size. Thus for the limiting case $m_1 = m_2$ the upper curve has been artificially 'folded back' from that part of the Brillouin zone where $\pi/2a < k \leq \pi/a$, as shown in Figure 6.

3. THREE-DIMENSIONAL CRYSTAL LATTICE

3.1 Normal mode frequencies in three dimensions

The biggest problem in generalizing the previous treatment to three dimensions is that the force constants become considerably more complicated, because the force on each atom due to displacement of its neighbours is a vector. Consider first how equation (1) for the force in one dimension may be rewritten:

$$F_0 = \sum_{l \neq 0} \gamma_l (u_l - u_0) = \sum_{l \neq 0} \gamma_l u_l - \sum_{l \neq 0} \gamma_l u_0. \quad (22)$$

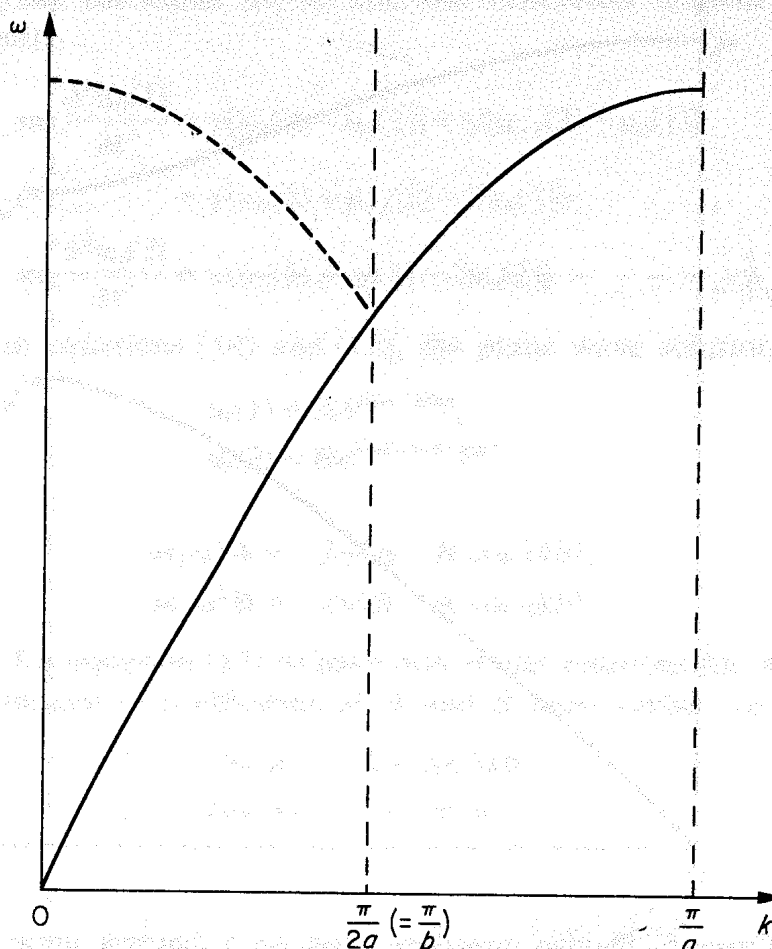


Figure 6. The true phonon dispersion curve for a monatomic linear chain (solid line) and when treated as the limiting case $m_1 = m_2$ for a diatomic linear chain (broken line), in which case the Brillouin zone is artificially reduced in size

If we define a special quantity γ_0 as $\gamma_0 = -\sum_{l \neq 0} \gamma_l$, F_0 reduces to

$$F_0 = \sum_{l=-\infty}^{+\infty} \gamma_l u_l. \quad (23)$$

The physical significance of γ_0 is simply that it represents the restoring force constant on the atom at the origin due to a displacement of itself.

In three dimensions, equation (23) can be generalized to

$$\mathbf{F}_0 = -\sum_l \Phi_l \cdot \mathbf{u}_l, \quad (24)$$

(the minus sign is introduced simply for convenience, because Φ then represents the second derivative of the equilibrium crystal potential energy) and the problem, which must be solved for the particular type of crystal

structure under consideration, is to relate the tensor Φ to the various force constants between neighbouring atoms.

If we use α and β as coefficients to represent the Cartesian components of the vectors, the force equation (24) can be written

$$F_{0,\alpha} = - \sum_l \sum_{\beta=1}^3 \Phi_{l,\alpha\beta} u_{l,\beta}, \quad \alpha = 1, 2, 3. \quad (25)$$

There are now three equations of motion for each atom, corresponding to the three degrees of freedom:

$$m \frac{\partial^2}{\partial t^2} u_{0,\alpha} = - \sum_l \sum_{\beta=1}^3 \Phi_{l,\alpha\beta} u_{l,\beta} \quad (26)$$

and the three-dimensional form of a plane wave is

$$u_{l,\alpha}(\mathbf{k}) = A_\alpha \exp[i(\omega t - \mathbf{k} \cdot \mathbf{r}_l)], \quad (27)$$

for a wave travelling in the direction of \mathbf{k} , where \mathbf{r}_l is the position vector of the l th atom. The precise form of \mathbf{r}_l will depend on the crystal structure.

To facilitate the generalization to a unit cell containing more than one atom, it is convenient at this point to make two new definitions:

$$B_\alpha = m^{1/2} A_\alpha, \quad \mathcal{D}_{\alpha\beta} = \frac{1}{m} \sum_l \Phi_{l,\alpha\beta} \exp(-i\mathbf{k} \cdot \mathbf{r}_l). \quad (28)$$

Using these quantities, substitution of equation (27) into the equations of motion (26) gives

$$\omega^2 B_\alpha = \sum_{\beta=1}^3 \mathcal{D}_{\alpha\beta} B_\beta, \quad \alpha = 1, 2, 3, \quad (29)$$

or in matrix form:

$$\omega^2 \mathbf{B} = \mathcal{D} \cdot \mathbf{B}. \quad (30)$$

This is a typical eigenvalue problem, and the solutions for ω^2 are the roots of the determinantal equation

$$\text{Det}(\mathcal{D} - \omega^2 \mathbf{I}) = 0. \quad (31)$$

The matrix \mathcal{D} is commonly called the *dynamical matrix*, and the determinant is called the *secular determinant*.

It is interesting to note that, as might be expected, for the case of \mathbf{k} in a symmetry direction the solutions (i.e. the normal modes of vibration) correspond to one longitudinal wave and two transverse waves (often degenerate). For non-symmetry directions, however, the normal modes do not necessarily have such a simple form.

Let us consider as an example the unit displacement of atom 1 in the x -, y - or z -direction. In each case this results in a radial component of displacement of $1/\sqrt{3}$, and since only radial forces are being considered, the resultant force on atom 0 is $(1/\sqrt{3})\gamma$. If we in turn resolve this force into its three Cartesian components, these can be written as $F_{0,x} = F_{0,y} = F_{0,z} = \frac{1}{3}\gamma$. Thus each Cartesian component of force due to unit displacement along any Cartesian axis is $\frac{1}{3}\gamma$, and this means that $-\Phi_{1,\alpha\beta} = \frac{1}{3}\gamma$ for all α and β . Thus

$$-\Phi_1 = \frac{1}{3}\gamma \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}. \quad (33)$$

Exactly the same will be true for atom 5, in the $[\bar{1}\bar{1}\bar{1}]$ -direction, i.e.

$$-\Phi_5 = -\Phi_1. \quad (34)$$

For the remaining atoms, along $[\bar{1}11]$ -, $[1\bar{1}1]$ -, and $[11\bar{1}]$ -directions and their opposite neighbours, the matrices are respectively

$$\begin{aligned} -\Phi_2 = -\Phi_6 &= \frac{1}{3}\gamma \begin{pmatrix} 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & 1 \end{pmatrix}, & -\Phi_3 = -\Phi_7 &= \frac{1}{3}\gamma \begin{pmatrix} 1 & -1 & 1 \\ -1 & 1 & -1 \\ 1 & -1 & 1 \end{pmatrix}, \\ -\Phi_4 = -\Phi_8 &= \frac{1}{3}\gamma \begin{pmatrix} 1 & 1 & -1 \\ 1 & 1 & -1 \\ -1 & -1 & 1 \end{pmatrix}. \end{aligned} \quad (35)$$

The second-nearest neighbours lie on the six faces of a cube of side $4a$. Thus for atom 9, lying along the $[100]$ -direction, a unit displacement in the x -direction gives a force $R\gamma$ in that direction on the atom at 0, and orthogonal displacements have no effect. Thus the only non-zero matrix elements are

$$-\Phi_{9,xx} = -\Phi_{12,xx} = -\Phi_{10,yy} = -\Phi_{13,yy} = -\Phi_{11,zz} = -\Phi_{14,zz} = R\gamma. \quad (36)$$

Finally we must calculate Φ_0 . Now this is simply the force on atom 0 due to unit displacement of itself. Thus a unit displacement of 0 along $0x$ is equivalent to a displacement of all the neighbours along $-0x$. Adding the components of force due to all the other atoms, we find

$$-\Phi_{0,xx} = -\frac{8}{3}\gamma - 2R\gamma, \quad -\Phi_{0,xy} = 0, \quad -\Phi_{0,xz} = 0, \text{ etc.} \quad (37)$$

Thus

$$-\Phi_0 = -2\gamma\left(\frac{4}{3} + R\right) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (38)$$