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Properties of Nearly Perfect Crystals at Very Low Temperatures

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Harmonic and Anharmonic Properties of Diamond Structure Crystals with Application to the Calculation of the Thermal Expansion of Silicon

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy

in Physics

by

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"Theory of Negative Grüneisen Parameters and Thermal Expansion of Silicon", K.H. Wanser and R.F. Wallis, Bull. Am. Phys. Soc. 26, 312 (1981).

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ABSTRACT OF THE DISSERTATION

Harmonic and Anharmonic Properties of Diamond Structure Crystals with Application to the Calculation of the Thermal Expansion of Silicon

by

Keith Herbert Wanser

Doctor of Philosophy in Physics
University of California, Irvine, 1982
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Silicon has interesting harmonic and anharmonic properties such as the low-lying transverse acoustic modes at the X and L points of the Brillouin zone, negative Grüneisen parameters, negative thermal expansion and anomalous acoustic attenuation. In an attempt to understand these properties, a lattice dynamical model employing long-range, nonlocal, dipole-dipole interactions has been developed. Several interesting features of this interaction are found and discussed. Analytic expressions for the Grüneisen parameters of several modes are presented. These expressions explain how the negative Grüneisen parameters arise. It is found that short-range anharmonicity is inadequate to explain the experimental data for the Grüneisen parameters. Application of this model to the calculation of the thermal expansion of silicon from 5K to 1700K is made. Good agreement with experiment is obtained from 17K to the melting point. The thermoelastic contribution to the acoustic attenuation of silicon is computed from 1-300K . Strong attenuation anomalies associated with negative thermal expansion are found in the vicinity of 17K and 125K . Electrostatic multipole interaction energies in a nonlocal dielectric medium and the Ewald method and its application to dipole sums are discussed in detail in the appendices.

INTRODUCTION

The present study was motivated by a desire to understand the acoustic attenuation of silicon at low frequency and low temperature. Professor Joseph Weber reported[1] an interesting narrow dip in the mechanical quality factor or Q of a large, (~1 meter long) nearly perfect, single crystal of silicon in the vicinity of 12K at 3.4KHz. The extremely large Q of such crystals,[2] of the order of 10^9, caused them to be of interest as possible gravitational wave detectors or ultrastable clocks.

Existing anharmonic calculations and measurements[3] at 300-500 MHz show no peak in the acoustic attenuation of silicon at low temperature. Studies of impurity induced attenuation[4] showed this mechanism to be unlikely, since the dip in Q was too narrow to be fit by a relaxation type expression with an activated relaxation time. Furthermore, the boron impurity content of the silicon crystal was 8×10^{14} atoms/cm^3, a rather low impurity concentration.

After considering several possible attenuation mechanisms, the author became aware of the negative thermal expansion of silicon. A calculation of the thermoelastic contribution to the acoustic attenuation of silicon showed strong attenuation anomalies near 13K and 17K due to the change in sign of the thermal expansion coefficient. This calculation, together with earlier studies, suggests that the anomaly in the Q is an anharmonic effect and not due to impurities.

Since third order elasticity theory is unable to yield the negative thermal expansion of silicon,[5] it was realized that elasticity theory could give misleading results for anharmonic properties of diamond structure crystals. It was thus desireable to develop a realistic lattice dynamical model for harmonic and anharmonic properties of silicon. With this in mind, it was decided to calculate the thermal expansion of silicon.

Silicon has negative Grüneisen parameters for several modes and negative thermal expansion as a consequence of this. The early work of Barron[6] pointed out that an fcc crystal with only nearest neighbor Hooke's Law central potential interactions would have a thermal expansion that is negative at all temperatures. Blackman[7] considered an ionic lattice model with the zinc blende structure and found negative Grüneisen parameters in the elastic region. This work, while interesting, did not show how the negative mode gammas arise, and no analytic expressions for the mode gammas where given. Bienenstock[8] made a calculation of the thermal expansion of germanium but the approximations made were somewhat drastic and the physical mechanism for the negative mode gammas was not recognized. Also, no analytic expressions for the mode gammas were presented. Similar criticisms apply to the calculations of Dolling and Cowley[9] and Jex,[10] as discussed in detail in Chapter 2.

In Chapter 1 we develop the harmonic lattice dynamical model, including the investigation of long-range nonlocal dipole interactions. In Chapter 2 we develop the anharmonic model, which is a consistent extension of the harmonic model. Analytic expressions for the Grüneisen parameters of several modes are presented and the model applied to a calculation of the thermal expansion of silicon. In Chapter 3 we present a calculation of the anomalous thermoelastic attenuation in silicon and in Chapter 4 a summary of conclusions is given. Several details pertaining to the discussion in Chapters 1 and 2 are given in the appendices.

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Chapter 1

Harmonic Lattice Dynamics of the Diamond Structure

> "O Lord, how manifold are thy works!
> in wisdom hast thou made them all:
> the earth is full of thy riches."
>
> Psalm 104:24

INTRODUCTION

In this chapter we develop a model for the harmonic lattice dynamics of diamond structure crystals. The chapter is divided into four main sections. First we discuss some elementary properties of the diamond structure. Second, we develop a model for the short-range contributions to the dynamical matrix. Third, we develop a model for the long-range contribution to the dynamical matrix employing nonlocal dipoles. This is a lengthy section and requires several side discussions to be found in the appendices. Fourth, we present analytic expressions for the elastic constants and for phonon frequencies along symmetry directions using the model developed in the previous two sections. We also present fits to experimental data and phonon dispersion curves for silicon in this section.

Figure 1. The diamond crystal structure showing the tetrahedral bond arrangement.

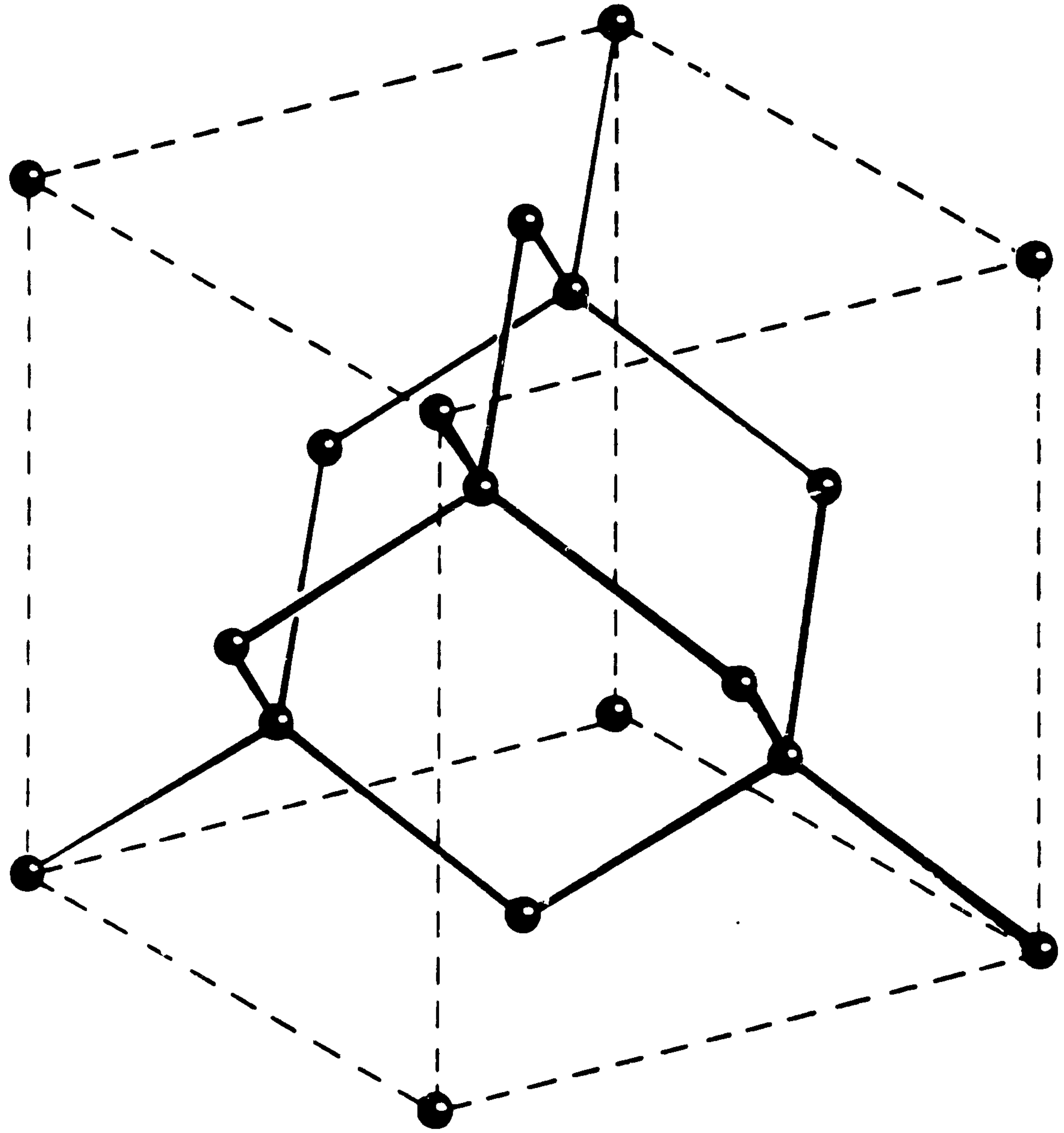
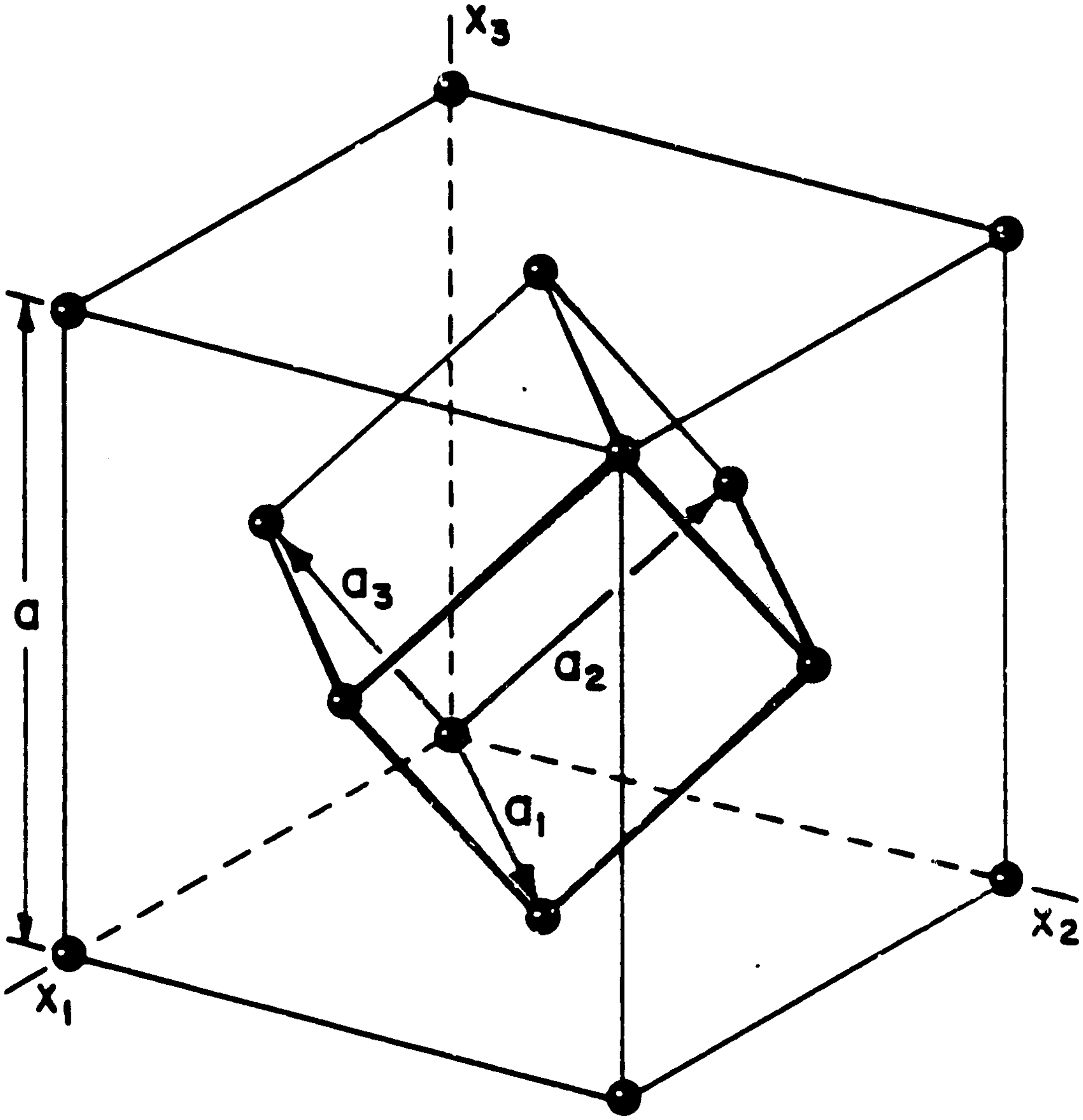


Figure 2. The rhombohedral primitive cell of the face-centered cubic lattice. The primitive translation vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ connect the lattice point at the origin with the lattice points at the face centers. Shown are conventions used in the present work.



x_3
a_3
a_2
a_1
a
x_1
x_2

DIAMOND STRUCTURE

The purpose of this section is to define some conventions that will be used throughout this thesis, as well as acquaint the reader with some basic properties of the diamond structure.

The diamond structure is a face-centered cubic space lattice with two atoms per unit cell.[1] (see Fig. 1) It may be visualized as two interpenetrating fcc lattices with one shifted relative to the other by one quarter of the body diagonal of the conventional cube. The lattice position vectors are given by

$$\vec{R}(\ell\kappa) = \vec{R}(\ell) + \vec{R}(\kappa) \ , \tag{1.1}$$

with Bravais lattice vectors

$$\vec{R}(\ell) = \ell_1\vec{a}_1 + \ell_2\vec{a}_2 + \ell_3\vec{a}_3 \ , \tag{1.2}$$

and the basis vectors

$$\vec{R}(\kappa) = \frac{\kappa}{4}(\vec{a}_1 + \vec{a}_2 + \vec{a}_3) \quad \text{for} \quad \kappa = 0,1 \ . \tag{1.3}$$

Here ℓ_1, ℓ_2, ℓ_3 are arbitrary integers. The primitive translation vectors $\vec{a}_i$ are given in terms of the cartesian unit vectors $\hat{e}_i$ by

$$\vec{a}_1 = \frac{a}{2}(\hat{e}_1 + \hat{e}_2) \tag{1.4a}$$

$$\vec{a}_2 = \frac{a}{2}(\hat{e}_2 + \hat{e}_3) \tag{1.4b}$$

$$\vec{a}_3 = \frac{a}{2}(\hat{e}_1 + \hat{e}_3) \tag{1.4c}$$

where a is the conventional cube edge which is 5.430Å for silicon at 300K.[2] (see Fig. 2) Thus we have in terms of cartesian coordinates

$$\vec{R}(\ell\kappa) = \frac{a}{2}[(\ell_1 + \ell_3 + \kappa/2)\hat{e}_1 + (\ell_1 + \ell_2 + \kappa/2)\hat{e}_2 + (\ell_2 + \ell_3 + \kappa/2)\hat{e}_3] . \tag{1.5}$$

In the following we denote

$$\vec{R}(\ell\kappa|\ell'\kappa') = \vec{R}(\ell\kappa) - \vec{R}(\ell'\kappa') . \tag{1.6}$$

The volume of the primitive cell is

$$\Omega_o = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)| = \frac{a^3}{4} , \tag{1.7}$$

and the mass density of the perfect crystal is

$$\rho = \frac{2M}{\Omega_o} = \frac{8M}{a^3} , \tag{1.8}$$

where M is the mass of the atom.

For the first few neighbors of a given atom we have the following.

$r_o = \frac{\sqrt{3}\,a}{4}$ = first neighbor distance

4 first neighbors, (1.9a)

$r_2 = \frac{a}{\sqrt{2}} = 1.6329932\ r_o$ = second neighbor distance

12 second neighbors, (1.9b)

$r_3 = \frac{\sqrt{11}\, a}{4} = 1.9148542\ r_o$ = third neighbor distance

12 third neighbors, (1.9c)

$r_4 = a = 2.3094011\ r_o$ = fourth neighbor distance

6 fourth neighbors. (1.9d)

Thus we see that the fourth neighbor distance is the first to exceed twice the nearest neighbor distance. The tetrahedral bond angle is given by (see section on angle bending)

$$\theta^{(o)} = \cos^{-1}(-1/3) = 109.47122^\circ \ . \qquad (1.10)$$

This is the angle defined by a given atom and any two of its nearest neighbors, when in the equilibrium positions.

We now discuss the reciprocal lattice. The reciprocal lattice to the face-centered cubic lattice is the body-centered cubic lattice.[3] The reciprocal lattice vectors are given by

$$\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3 \qquad (1.11)$$

with m_1, m_2, m_3 arbitrary integers. The primitive translation vectors $\vec{b}_i$ of the reciprocal lattice are given in terms of the cartesian unit vectors $\hat{e}_i$ by

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{e}_1 + \hat{e}_2 - \hat{e}_3) \quad (1.12a)$$

$$\vec{b}_2 = \frac{2\pi}{a}(-\hat{e}_1 + \hat{e}_2 + \hat{e}_3) \quad (1.12b)$$

$$\vec{b}_3 = \frac{2\pi}{a}(\hat{e}_1 - \hat{e}_2 + \hat{e}_3) \ . \quad (1.12c)$$

Thus we have in terms of cartesian coordinates

$$\vec{G} = \frac{2\pi}{a}[(m_1 - m_2 + m_3)\hat{e}_1 + (m_1 + m_2 - m_3)\hat{e}_2 + (-m_1 + m_2 + m_3)\hat{e}_3] \ . \quad (1.13)$$

Just as we have a primitive cell in real space, we also have a primitive cell in reciprocal space. This minimum volume cell is called the first Brillouin zone. It is the Wigner-Seitz cell in reciprocal space. Figure 3 shows the first Brillouin zone of the face-centered cubic crystal lattice.

At this point it is appropriate to make a brief comment on the stability of the diamond structure. Carbon, silicon, germanium and grey tin crystallize in the diamond structure. The first-order semiconductor to metal transition occurring in tin at 286K and atmospheric pressure is accompanied by a change in structure from the diamond cubic (grey, α-Sn) to the body-centered tetragonal (white, β-Sn) form.[4] This transition has been observed in silicon, germanium and a number of III-V compounds at high pressures.[5] For silicon, a sudden drop in resistivity of over five orders of magnitude is observed in the vicinity of 120-150 kbar.[4]

Other crystal forms have also been found. A metastable, semiconducting, hexagonal diamond ("Wurtzite") structure has been observed for carbon and silicon[6], as well as a metallic, body-centered cubic structure for silicon.[4,5] Electronic structure calculations for silicon[7] have shown that the diamond structure is the lowest in energy for a number of plausible crystal structures. (see Fig. 4) The next structure lowest in energy is the hexagonal diamond and then the β-tin structure. By way of contrast, above ~-100°C ice Ih, which is the hexagonal diamond structure for the oxygens, is more stable than ice Ic, which is the ordinary diamond structure.[8] It appears that the two structures for ice are very close in energy, as they are for silicon as shown in Fig. 4. The reason for this is that the tetrahedral coordination is preserved and the nearest neighbor distance is essentially the same for the two structures. The second neighbor distances are also the same, but the orientation of the second neighbor position vectors differ between the two structures.

Figure 3. First Brillouin zone of the face-centered cubic lattice with symmetry points and lines labeled.

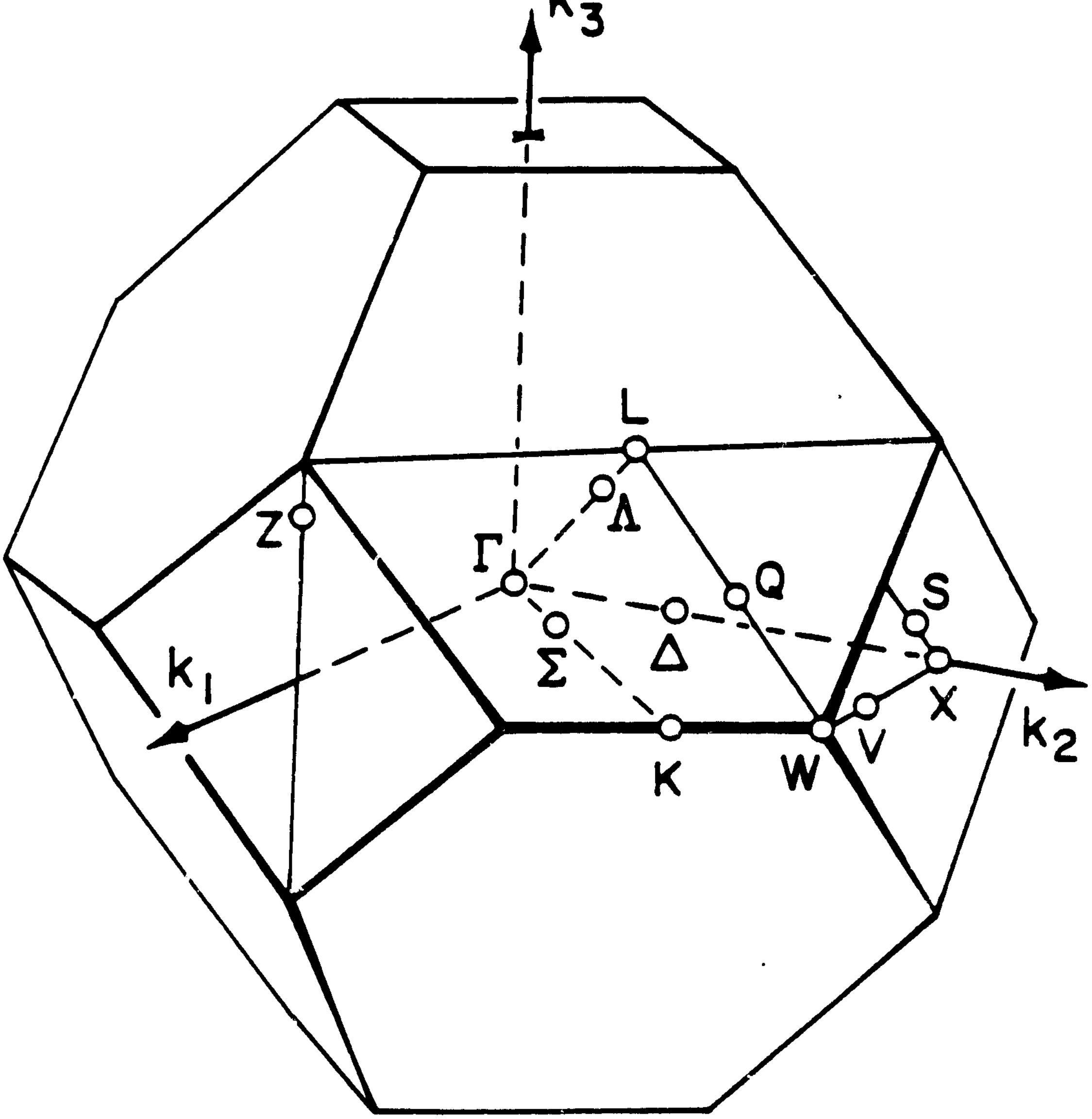
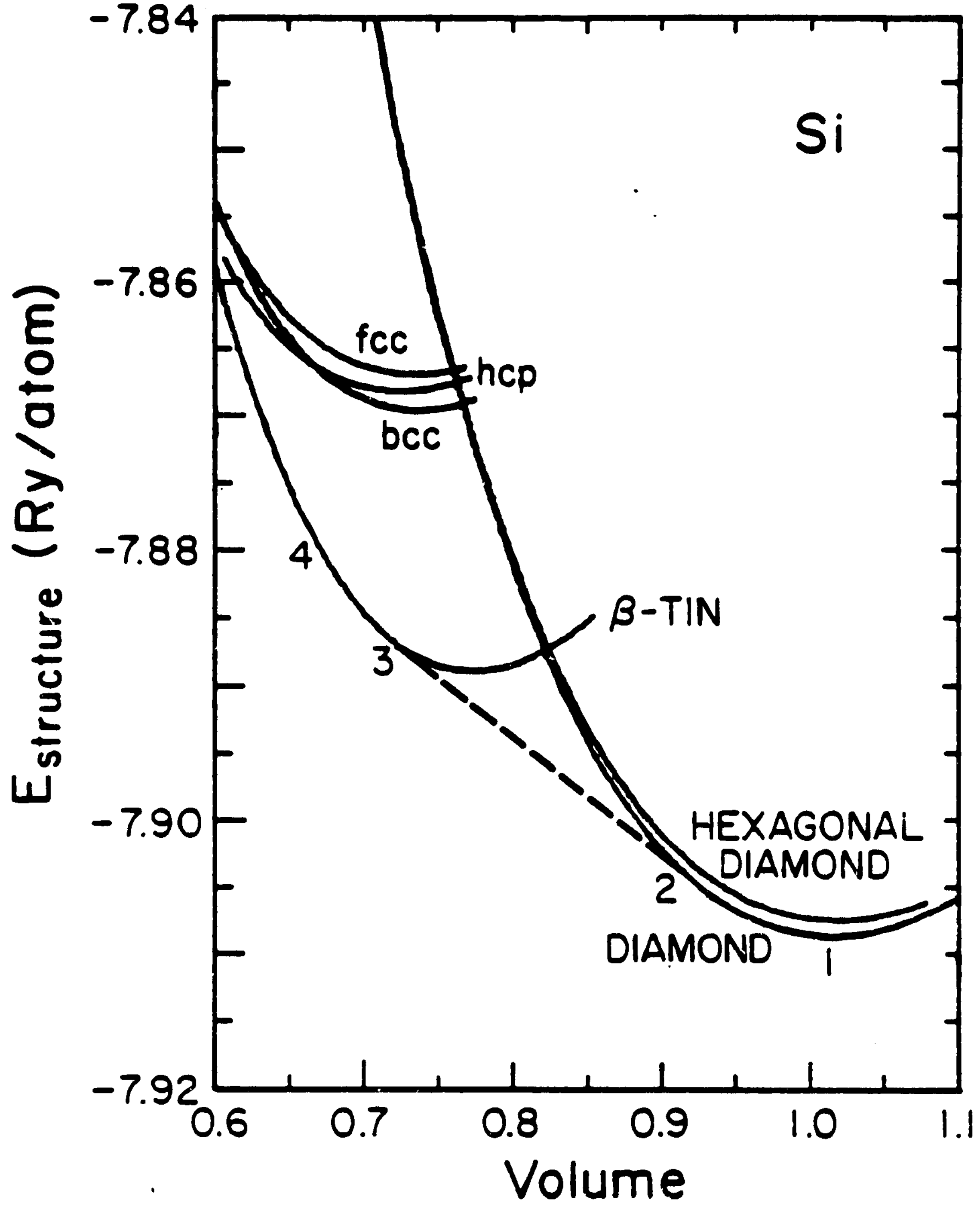

k_3
L
Λ
Z
Γ
Q
S
Δ
Σ
k_1
X
k_2
K
W
V

Figure 4. The diamond, hexagonal diamond, β-tin, hcp, bcc, and fcc structural energies (in units of Ry/atom) as a function of the atomic volume (normalized to the measured free volume) for Si. The dashed line is the common tangent of the energy curves for the diamond and the β-tin structures. (Courtesy M.T. Yin, Ref. 7)


Si
fcc
hcp
bcc
β-TIN
HEXAGONAL DIAMOND
DIAMOND
1
2
3
4
E_structure (Ry/atom)
-7.84
-7.86
-7.88
-7.90
-7.92
0.6
0.7
0.8
0.9
1.0
1.1
Volume

HARMONIC APPROXIMATION AND EQUATIONS OF MOTION

Before constructing the harmonic model, a few words concerning the harmonic approximation and equations of motion are in order. The harmonic hamiltonian is

$$H_o = T + \Phi_2 \tag{1.14}$$

where T is the kinetic energy and Φ_2 is the contribution to the crystal potential energy which is quadratic in the nuclear displacements. Thus we have for the diamond structure

$$T = \sum_{\ell\kappa\alpha} \frac{P_\alpha^2(\ell\kappa)}{2M} , \tag{1.15}$$

and

$$\Phi_2 = \frac{1}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')u_\alpha(\ell\kappa)u_\beta(\ell'\kappa') , \tag{1.16}$$

with

$$\Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \left.\frac{\partial^2\Phi}{\partial u_\alpha(\ell\kappa)\partial u_\beta(\ell'\kappa')}\right|_o . \tag{1.17}$$

Here we have denoted $P_\alpha(\ell\kappa)$ and $u_\alpha(\ell\kappa)$ as the α cartesian component of the momentum and displacement, respectively, of atom $(\ell\kappa)$. Note that $u_\alpha(\ell\kappa)$ is measured from the rest position specified by Eq. (1.1). The $\Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')$ are known as the second order atomic force constants. Φ is the potential energy of the crystal as a function of the nuclear displacements and the derivatives in Eq. (1.17) are to be evaluated with all atoms in the rest positions. Using the Hamiltonian Eq. (1.14), one can show that the equations of motion are

$$M\ddot{u}_{\alpha}(\ell\kappa) = -\sum_{\ell'\kappa'\beta}\Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')u_{\beta}(\ell'\kappa') \ . \qquad (1.18)$$

This equation holds classically and also quantum mechanically, as can be verified by using the equal time commutation relations for $P_{\alpha}(\ell\kappa)$ and $u_{\alpha}(\ell\kappa)$ as well as the Heisenberg equation of motion.

If we now seek normal mode solutions of the form

$$u_{\alpha}(\ell\kappa) = \frac{W_{\alpha}(\kappa)}{\sqrt{M}}e^{i\vec{k}\cdot\vec{R}(\ell)-i\omega t} \ , \qquad (1.19)$$

where $\vec{k}$ is the wavevector and ω is the frequency, then Eq. (1.18) becomes

$$\omega^2 W_{\alpha}(\kappa) = \sum_{\beta\kappa'}D_{\alpha\beta}(\kappa\kappa'|\vec{k})W_{\beta}(\kappa') \ , \qquad (1.20)$$

where $D_{\alpha\beta}(\kappa\kappa'|\vec{k})$ is the dynamical matrix defined by

$$D_{\alpha\beta}(\kappa\kappa'|\vec{k}) = \frac{1}{M}\sum_{\ell'}\Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')e^{-i\vec{k}\cdot[\vec{R}(\ell)-\vec{R}(\ell')]} . \qquad (1.21)$$

Note that in this thesis we will be using the first form of the dynamical matrix, Eq. (1.21), as opposed to the second form of the dynamical matrix.[9] The two differ by a $\vec{k}$ dependent phase factor.

Using the invariance of the force constants under a crystal lattice translation $\vec{R}(m)^{10}$ we have

$$\Phi_{\alpha\beta}(\ell+m,\kappa|\ell'+m,\kappa') = \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') \ . \qquad (1.22)$$

Letting $m = -\ell$ in Eq. (1.22) gives

$$\Phi_{\alpha\beta}(0,\kappa|\ell'-\ell,\kappa') = \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') \ . \qquad (1.23)$$

Thus Eq. (1.21) can be written as

$$D_{\alpha\beta}(\kappa\kappa'|\vec{k}) = \frac{1}{M}\sum_{\ell'} \Phi_{\alpha\beta}(0,\kappa|\ell'-\ell,\kappa')e^{i\vec{k}\cdot[\vec{R}(\ell')-\vec{R}(\ell)]} \ . \qquad (1.24)$$

Neglecting surface effects, we can relabel the sum in Eq. (1.24) so that

$$D_{\alpha\beta}(\kappa\kappa'|\vec{k}) = \frac{1}{M}\sum_{m} \Phi_{\alpha\beta}(0,\kappa|m,\kappa')e^{i\vec{k}\cdot\vec{R}(m)} \ . \qquad (1.25)$$

From Eq. (1.25) we see that the dynamical matrix is independent of the unit cell index ℓ in Eq. (1.21).

Since the order of partial differentiation is interchangeable, we have from Eq. (1.17) the "flip" symmetry property

$$\Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \Phi_{\beta\alpha}(\ell'\kappa'|\ell\kappa) \ . \qquad (1.26)$$

Using this fact plus translational symmetry, Eq. (1.22), one has the Hermitian property

$$D_{\alpha\beta}(\kappa\kappa'|\vec{k}) = D^{*}_{\beta\alpha}(\kappa'\kappa|\vec{k}) \ , \tag{1.27}$$

where the * denotes complex conjugate. From the definition Eq. (1.21) we also have

$$D^{*}_{\alpha\beta}(\kappa\kappa'|\vec{k}) = D_{\alpha\beta}(\kappa\kappa'|-\vec{k}) \ . \tag{1.28}$$

Now for the diamond structure, $D_{\alpha\beta}(\kappa\kappa'|\vec{k})$ is a 6×6 Hermitian matrix. Thus it will have six real eigenvalues for each value of $\vec{k}$. The eigenvalues we label $\omega^2(\vec{k}j)$, where $j = 1,2,\cdots,6$ denotes the branch index. Furthermore, to each value of $\vec{k}$ we can find a complete orthonormal set of eigenvectors $e_\alpha(\kappa|\vec{k}j)$ that obey the eigenvalue equation

$$\omega^2(\vec{k}j)e_\alpha(\kappa|\vec{k}j) = \sum_{\beta\kappa'} D_{\alpha\beta}(\kappa\kappa'|\vec{k})e_\beta(\kappa'|\vec{k}j) \ , \tag{1.29}$$

the orthonormality property

$$\sum_{\kappa\alpha} e^{*}_\alpha(\kappa|\vec{k}j)e_\alpha(\kappa|\vec{k}j') = \delta_{jj'} \ , \tag{1.30}$$

and the completeness relation

$$\sum_{j} e_\alpha(\kappa|\vec{k}j)e_\beta(\kappa'|\vec{k}j) = \delta_{\alpha\beta}\delta_{\kappa\kappa'} \ . \tag{1.31}$$

Without loss of generality we also have the following properties, which correspond to a particular set of phase and branch labeling conventions[12]

$$\omega(\vec{k}j) = \omega(-\vec{k}j) \; , \tag{1.32}$$

$$e_\alpha(\kappa|\vec{k}j) = e^*_\alpha(\kappa|-\vec{k}j) \; . \tag{1.33}$$

With these preliminaries out of the way, we can derive some properties of the force constants and dynamical matrix imposed by inversion symmetry plus translation invariance.

Now consider the effect of a crystal symmetry operation represented by $\{S|\vec{v}(S)+\vec{R}(m)\}$. Applied to the position vector given by Eq. (1.1), this operation transforms it as

$$\begin{aligned}\{S|\vec{v}(S)+\vec{R}(m)\}\vec{R}(\ell\kappa) &= \overleftrightarrow{S}\cdot\vec{R}(\ell\kappa) + \vec{v}(S) + \vec{R}(m) \\ &\equiv \vec{R}(LK) \; . \end{aligned} \tag{1.34}$$

$\overleftrightarrow{S}$ 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 smaller than any primitive translation vector of the crystal, and $\vec{R}(m)$ is one of the translation vectors, Eq. (1.2). For a review of crystal symmetry operations, we refer the reader to the article by Maradudin and Vosko[13] and the book by Lax.[14] Furthermore, the invariance of the potential energy under the operation $\{S|\vec{v}(S)+\vec{R}(m)\}$ produces the transformation law for the second order force constants

$$\Phi_{\mu\nu}(LK|L'K') = \sum_{\alpha\beta} S_{\mu\alpha}S_{\nu\beta}\Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') \ . \qquad (1.35)$$

For the inversion operation we have[15]

$$S_{\alpha\beta} = -\delta_{\alpha\beta} \qquad (1.36a)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta symbol,

$$\vec{v}(S) = \vec{R}(1) = a/4(\hat{e}_1+\hat{e}_2+\hat{e}_3) \ , \qquad (1.36b)$$

and

$$\vec{R}(m) = 0 \ . \qquad (1.36c)$$

Thus from Eq. (1.34) the position vector is taken into

$$\vec{R}(LK) = -\vec{R}(\ell\kappa) + \vec{R}(1) \qquad (1.37)$$

so that in particular

$$\vec{R}(L,1) = -\vec{R}(\ell,0) + \vec{R}(1) = \vec{R}(-\ell,1) \qquad (1.38a)$$

$$\vec{R}(L,0) = -\vec{R}(\ell,1) + \vec{R}(1) = \vec{R}(-\ell,0) \ . \qquad (1.38b)$$

Therefore the effect of the inversion operation is to interchange the sublattice labels $\kappa = 0,1$ and take $\vec{R}(\ell)$ into $-\vec{R}(\ell)$. This point will be important later in the section on nonlocal dipoles. Thus for the inversion operation applied to the force constants, Eq. (1.35) becomes

$$\Phi_{\alpha\beta}(LK|L'K') = \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') \ , \qquad (1.39)$$

or more explicitly using Eq. (1.38)

$$\Phi_{\alpha\beta}(\ell,0|\ell',0) = \Phi_{\alpha\beta}(-\ell,1|-\ell',1) \qquad (1.40a)$$

$$\Phi_{\alpha\beta}(\ell,0|\ell',1) = \Phi_{\alpha\beta}(-\ell,1|-\ell',0) \qquad (1.40b)$$

$$\Phi_{\alpha\beta}(\ell,1|\ell',0) = \Phi_{\alpha\beta}(-\ell,0|-\ell',1) \qquad (1.40c)$$

$$\Phi_{\alpha\beta}(\ell,1|\ell',1) = \Phi_{\alpha\beta}(-\ell,0|-\ell',0) \ . \qquad (1.40d)$$

Schematically, we can write the dynamical matrix, Eq. (1.21), in block form

$$[D_{\alpha\beta}(\kappa\kappa'|\vec{k})] = \left[\begin{array}{c|c} D_{\alpha\beta}(0,0|\vec{k}) & D_{\alpha\beta}(0,1(\vec{k}) \\ \hline D_{\alpha\beta}(1,0|\vec{k}) & D_{\alpha\beta}(1,1|\vec{k}) \end{array}\right] \ . \qquad (1.41)$$

The Hermitian property, Eq. (1.27), is

$$D_{\alpha\beta}(0,0|\vec{k}) = D^{*}_{\beta\alpha}(0,0|\vec{k}) \qquad (1.42a)$$

$$D_{\alpha\beta}(1,1|\vec{k}) = D^{*}_{\beta\alpha}(1,1|\vec{k}) \qquad (1.42b)$$

$$D_{\alpha\beta}(0,1|\vec{k}) = D^{*}_{\beta\alpha}(1,0|\vec{k}) \ . \qquad (1.42c)$$

Consider

$$D_{\alpha\beta}(1,1|\vec{k}) = \frac{1}{M}\sum_{\ell'} \Phi_{\alpha\beta}(\ell,1|\ell',1)e^{-i\vec{k}\cdot[\vec{R}(\ell)-\vec{R}(\ell')]} \qquad (1.43a)$$

using Eq. (1.40d) we have

$$D_{\alpha\beta}(1,1|\vec{k}) = \frac{1}{M}\sum_{\ell'} \Phi_{\alpha\beta}(-\ell,0|-\ell',0)e^{-i\vec{k}\cdot[\vec{R}(\ell)-\vec{R}(\ell')]} \qquad (1.43b)$$

using lattice translation symmetry, Eq. (1.22), and relabeling the summation variables we obtain

$$D_{\alpha\beta}(1,1|\vec{k}) = D^{*}_{\alpha\beta}(0,0|\vec{k}) \ . \qquad (1.44)$$

Consider next

$$D_{\alpha\beta}(1,0|\vec{k}) = \frac{1}{M}\sum_{\ell'} \Phi_{\alpha\beta}(\ell,1|\ell',0)e^{-i\vec{k}\cdot[\vec{R}(\ell)-\vec{R}(\ell')]} , \qquad (1.45)$$

using Eq. (1.40c) we have

$$D_{\alpha\beta}(1,0|\vec{k}) = \frac{1}{M} \sum_{\ell'} \Phi_{\alpha\beta}(-\ell,0|-\ell',1)e^{-i\vec{k}\cdot[\vec{R}(\ell)-\vec{R}(\ell')]} \tag{1.46}$$

again using lattice translation symmetry plus relabeling the summation variables we obtain

$$D_{\alpha\beta}(1,0|\vec{k}) = D^{*}_{\alpha\beta}(0,1|\vec{k}) \ . \tag{1.47}$$

Combining Eqs. (1.42c) and (1.47) we further obtain that

$$D_{\alpha\beta}(0,1|\vec{k}) = D_{\beta\alpha}(0,1|\vec{k}) \ . \tag{1.48}$$

In summary, the form of the dynamical matrix is reduced to

$$[D_{\alpha\beta}(\kappa\kappa'|\vec{k})] = \left[\begin{array}{c|c} D_{\alpha\beta}(0,0|\vec{k}) & D_{\alpha\beta}(0,1|\vec{k}) \\ \hline D^{*}_{\alpha\beta}(0,1|\vec{k}) & D^{*}_{\alpha\beta}(0,0|\vec{k}) \end{array}\right] , \tag{1.49}$$

with $\overleftrightarrow{D}(0,0|\vec{k})$ Hermitian and $\overleftrightarrow{D}(0,1|\vec{k})$ symmetric.[16] This form holds for any lattice with two like atoms per unit cell that are interchanged by the inversion operation.

CONTRIBUTIONS TO THE DYNAMICAL MATRIX

Since the potential energy can be written as a sum of contributions from various types of interactions, the force constants Eq. (1.17) and the dynamical matrix Eq. (1.21) can also be written as a sum of contributions from the various interactions. This allows separate computation of the contribution to the dynamical matrix from each type of interaction, and the total dynamical matrix can then be obtained by summing the different contributions.

For the model considered here, we divide the potential energy into a short-range part and a long-range dipole-dipole part so that

$$\Phi_2 = \Phi_2^{S.R.} + \Phi_2^{dd} , \qquad (1.50)$$

and we model the short-range contribution by

$$\Phi_2^{S.R.} = \Phi_2^{1^\circ} + \Phi_2^{2^\circ} + \Phi_2^{3^\circ} + \Phi_2^{4^\circ} + \Phi_2^{(\theta)} . \qquad (1.51)$$

Here $\Phi_2^{1^\circ}$, $\Phi_2^{2^\circ}$, $\Phi_2^{3^\circ}$ and $\Phi_2^{4^\circ}$ are the harmonic contributions to the potential energy from first, second, third and fourth neighbor central potential interactions, $\Phi_2^{(\theta)}$ is the harmonic contribution from nearest neighbor angle bending and Φ_2^{dd} is the harmonic part of the long-range, nonlocal dipole-dipole interaction energy.

Using the same notation, we label the contributions to the dynamical matrix

$$D_{\alpha\beta}(\kappa\kappa'|\vec{k}) = D_{\alpha\beta}^{S.R}(\kappa\kappa'|\vec{k}) + D_{\alpha\beta}^{dd}(\kappa\kappa'|\vec{k}) \ , \qquad (1.52)$$

with

$$D_{\alpha\beta}^{S.R.}(\kappa\kappa'|\vec{k}) = D_{\alpha\beta}^{1^\circ}(\kappa\kappa'|\vec{k}) + D_{\alpha\beta}^{2^\circ}(\kappa\kappa'|\vec{k}) + D_{\alpha\beta}^{3^\circ}(\kappa\kappa'|\vec{k}) + D_{\alpha\beta}^{4^\circ}(\kappa\kappa'|\vec{k}) + D_{\alpha\beta}^{(\theta)}(\kappa\kappa'|\vec{k}) \ . \qquad (1.53)$$

We now proceed to a discussion of the various terms in Eq. (1.53) and then the dipole-dipole part of Eq. (1.52).

CENTRAL POTENTIAL CONTRIBUTIONS TO THE DYNAMICAL MATRIX

For a two body central potential interaction, the potential only depends on the magnitude of the separation of the atoms. Denoting the potential for an atom of type κ interacting with an atom of type κ' at a distance r from it by $\phi_{\kappa\kappa'}(r)$, we can write the crystal potential energy due to central potentials as

$$\Phi_c = \frac{1}{2} \sum_{\ell\kappa} \sum_{\ell'\kappa'}{}' \phi_{\kappa\kappa'}(|\vec{R}(\ell\kappa|\ell'\kappa') + \vec{u}(\ell\kappa|\ell'\kappa')|) \ , \qquad (1.54)$$

where

$$\vec{u}(\ell\kappa|\ell'\kappa') = \vec{u}(\ell\kappa) - \vec{u}(\ell'\kappa') \ . \qquad (1.55)$$

The factor of 1/2 in front of the sum compensates for the fact that each interaction is counted twice in the sum, the prime on the second sum means exclude terms with $(\ell\kappa) = (\ell'\kappa')$.

Expanding the potential $\phi_{\kappa\kappa}(r)$ in powers of the displacements leads to

$$\begin{aligned}
\phi_{\kappa\kappa'}(|\vec{R}(\ell\kappa|\ell'\kappa') + \vec{u}(\ell\kappa|\ell'\kappa')|) &= \phi_{\kappa\kappa'}(|\vec{R}(\ell\kappa|\ell'\kappa')|) \\
&+ \sum_{\alpha} \phi_{\alpha}(\ell\kappa|\ell'\kappa')u_{\alpha}(\ell\kappa|\ell'\kappa') \\
&+ \frac{1}{2} \sum_{\alpha\beta} \phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')u_{\alpha}(\ell\kappa|\ell'\kappa')u_{\beta}(\ell\kappa|\ell'\kappa') \\
&+ \frac{1}{6} \sum_{\alpha\beta\gamma} \phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa')u_{\alpha}(\ell\kappa|\ell'\kappa')u_{\beta}(\ell\kappa|\ell'\kappa')u_{\gamma}(\ell\kappa|\ell'\kappa') \\
&+ \text{(higher order in displacements)}, \qquad (1.56)
\end{aligned}$$

with the expansion coefficients given by [17]

$$\phi_{\alpha}(\ell\kappa|\ell'\kappa') = \left[\frac{x_{\alpha}}{r}\,\phi'_{\kappa\kappa'}(r)\right]\Bigg|_{\vec{r}=\vec{R}(\ell\kappa|\ell'\kappa')} \tag{1.57a}$$

$$\phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \left\{\frac{x_{\alpha}x_{\beta}}{r^{2}}\left[\phi''_{\kappa\kappa'}(r) - \frac{1}{r}\,\phi'_{\kappa\kappa'}(r)\right] + \frac{\delta_{\alpha\beta}}{r}\,\phi'_{\kappa\kappa'}(r)\right\}\Bigg|_{\vec{r}=\vec{R}(\ell\kappa|\ell'\kappa')} \tag{1.57b}$$

$$\phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa') = \left\{\frac{x_{\alpha}x_{\beta}x_{\gamma}}{r^{3}}\left[\phi'''_{\kappa\kappa'}(r) - \frac{3\phi''_{\kappa\kappa'}(r)}{r} + \frac{3\phi'_{\kappa\kappa'}(r)}{r^{2}}\right] + \frac{x_{\alpha}\delta_{\beta\gamma}+x_{\beta}\delta_{\alpha\gamma}+x_{\gamma}\delta_{\alpha\beta}}{r^{2}}\left[\phi''_{\kappa\kappa'}(r) - \frac{1}{r}\,\phi'_{\kappa\kappa'}(r)\right]\right\}\Bigg|_{\vec{r}=\vec{R}(\ell\kappa|\ell'\kappa')} \tag{1.57c}$$

and

$$\vec{r} = \sum_{\alpha} x_{\alpha}\hat{e}_{\alpha} \ . \tag{1.57d}$$

Here we have denoted the derivatives by

$$\phi'(r) = \frac{d\phi(r)}{dr} \tag{1.58a}$$

$$\phi''(r) = \frac{d^{2}\phi(r)}{dr^{2}} \tag{1.58b}$$

$$\phi'''(r) = \frac{d^{3}\phi(r)}{dr^{3}} \ . \tag{1.58c}$$

Using Eqs. (1.54) and (1.56) we obtain the harmonic contribution to the crystal potential from central potentials

$$\Phi_{2c} = \frac{1}{4} \sum_{\ell\kappa\alpha} \sum_{\ell'\kappa'\beta}' \phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')u_\alpha(\ell\kappa|\ell'\kappa')u_\beta(\ell\kappa|\ell'\kappa') \ . \tag{1.59}$$

We now proceed to compute this for first, second, third and fourth neighbors.

FIRST NEIGHBOR CONTRIBUTION

Writing

$$\Phi_{2c} = \Phi_2^{1^\circ} + \Phi_2^{2^\circ} + \Phi_2^{3^\circ} + \Phi_2^{4^\circ} \qquad (1.60)$$

we have upon evaluating the sum in Eq. (1.59) over nearest neighbors

$$\Phi_2^{1^\circ} = \tfrac{1}{4} \sum_{\ell\alpha\beta} \sum_{i=1}^{4} \Big[\phi_{\alpha\beta}(\ell,0|\ell+\delta_i,1)u_\alpha(\ell,0|\ell+\delta_i,1)u_\beta(\ell,0|\ell+\delta_i,1)$$
$$+\phi_{\alpha\beta}(\ell,1|\ell+\delta_{i+4},0)u_\alpha(\ell,1|\ell+\delta_{i+4},0)u_\beta(\ell,1|\ell+\delta_{i+4},0)\Big] , \qquad (1.61)$$

where

$$\vec{\delta}_1 = 0 , \vec{\delta}_2 = -\vec{a}_1 , \vec{\delta}_3 = -\vec{a}_2 , \vec{\delta}_4 = -\vec{a}_3 \qquad (1.62a)$$

and

$$\vec{\delta}_{i+4} = -\vec{\delta}_i \quad \text{for} \quad 1 \leq i \leq 4 . \qquad (1.62b)$$

The $\vec{\delta}_i$ are the translation vectors to the unit cells of the nearest neighbors from the atom of interest. From the definition Eq. (1.57b) we have the lattice translation property

$$\phi_{\alpha\beta}(\ell+m,\kappa|\ell'+m,\kappa') = \phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') , \qquad (1.63)$$

and the further property that

$$\phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \phi_{\alpha\beta}(\ell'\kappa'|\ell\kappa) . \qquad (1.64)$$

Thus we have

$$\phi_{\alpha\beta}(\ell,0|\ell+\delta_i,1) = \phi_{\alpha\beta}(0,0|\delta_i,1) \tag{1.65a}$$

$$\phi_{\alpha\beta}(\ell,1|\ell+\delta_{i+4},0) = \phi_{\alpha\beta}(0,1|\delta_{i+4},0) \ , \tag{1.65b}$$

and further

$$\phi_{\alpha\beta}(\ell,1|\ell+\delta_{i+4},0) = \phi_{\alpha\beta}(0,0|\delta_i,1) \ . \tag{1.66}$$

Thus we can write Eq. (1.61) as

$$\Phi_2^{1^\circ} = \tfrac{1}{4} \sum_{\ell\alpha\beta} \sum_{i=1}^{4} \phi_{\alpha\beta}(0,0|\delta_i,1)\Big[u_\alpha(\ell,0|\ell+\delta_i,1)u_\beta(\ell,0|\ell+\delta_i,1) + u_\alpha(\ell,1|\ell-\delta_i,0)u_\beta(\ell,1|\ell-\delta_i,0)\Big] \ . \tag{1.67}$$

From the definition Eq. (1.57b) we can directly compute the four matrices $\phi_{\alpha\beta}(0,0|\delta_i,1)$. We exhibit them explicitly

$$\overleftrightarrow{\phi}(0,0|\delta_1,1) = \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix} \quad \overleftrightarrow{\phi}(0,0|\delta_2,1) = \begin{pmatrix} \alpha & \beta & -\beta \\ \beta & \alpha & -\beta \\ -\beta & -\beta & \alpha \end{pmatrix}$$

$$\overleftrightarrow{\phi}(0,0|\delta_3,1) = \begin{pmatrix} \alpha & -\beta & -\beta \\ -\beta & \alpha & \beta \\ -\beta & \beta & \alpha \end{pmatrix} \overleftrightarrow{\phi}(0,0|\delta_4,1) = \begin{pmatrix} \alpha & -\beta & \beta \\ -\beta & \alpha & -\beta \\ \beta & -\beta & \alpha \end{pmatrix} \tag{1.68}$$

where we have defined the force constants α and β as

$$\alpha = \left[\frac{1}{3}\,\phi_1''(r_o) + \frac{2}{3r_o}\,\phi_1'(r_o)\right] \tag{1.69a}$$

$$\beta = \left[\frac{1}{3}\,\phi_1''(r_o) - \frac{1}{3r_o}\,\phi_1'(r_o)\right] \ . \tag{1.69b}$$

For the sake of being explicit, we have labeled the nearest neighbor potential function $\phi_1(r)$. The derivatives are to be evaluated at the nearest neighbor distance Eq. (1.9a).

Since Eq. (1.18) can also be written as

$$M\ddot{u}_\alpha(\ell\kappa) = -\frac{\partial\Phi_2}{\partial u_\alpha(\ell\kappa)} , \tag{1.70}$$

if we now substitute the normal mode solution Eq. (1.19) into Eq. (1.20) we obtain the relation

$$\sum_{\beta\kappa'} D_{\alpha\beta}(\kappa\kappa'|\vec{k})W_\beta(\kappa') = \left\{ \frac{1}{\sqrt{M}}\left[\frac{\partial\Phi_2}{\partial u_\alpha(\ell\kappa)}\right] e^{-i\vec{k}\cdot\vec{R}(\ell)+i\omega t} \right\} , \tag{1.71}$$

where it is understood that we have substituted the normal mode solution after performing the derivative. Direct computation using Eq. (1.67) yields

$$\frac{\partial\Phi_2^{1^\circ}}{\partial u_\alpha(\ell,0)} = \sum_{i=1}^{4} \sum_{\beta} \phi_{\alpha\beta}(0,0|\delta_i,1)u_\beta(\ell,0|\ell+\delta_i,1) \tag{1.72a}$$

$$\frac{\partial\Phi_2^{1^\circ}}{\partial u_\alpha(\ell,1)} = \sum_{i=1}^{4} \sum_{\beta} \phi_{\alpha\beta}(0,0|\delta_i,1)u_\beta(\ell,1|\ell-\delta_i,0) . \tag{1.72b}$$

Using Eqs. (1.71) and (1.72) we obtain

$$D_{\alpha\beta}^{1^\circ}(0,0|\vec{k}) = \frac{1}{M}\sum_{i=1}^{4} \phi_{\alpha\beta}(0,0|\delta_i,1) , \tag{1.73a}$$

$$D^{1^\circ}_{\alpha\beta}(0,1|\vec{k}) = -\frac{1}{M}\sum_{i=1}^{4}\phi_{\alpha\beta}(0,0|\delta_i,1)e^{i\vec{k}\cdot\vec{\delta}_i} . \qquad (1.73b)$$

Using the matrices Eq. (1.68), we have more explicitly

$$\overleftrightarrow{D}^{1^\circ}(0,0|\vec{k}) = \frac{4\alpha}{M}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} . \qquad (1.73c)$$

SECOND NEIGHBOR CONTRIBUTION

Evaluating the sum in Eq. (1.59) over second nearest neighbors we obtain

$$\Phi_2^{2^\circ} = \frac{1}{4}\sum_{\ell\alpha\beta}\sum_{i=1}^{12}\Big[\phi_{\alpha\beta}(\ell,0|\ell+\mu_i,0)u_\alpha(\ell,0|\ell+\mu_i,0)u_\beta(\ell,0|\ell+\mu_i,0)$$

$$+\phi_{\alpha\beta}(\ell,1|\ell+\mu_{i+12},1)u_\alpha(\ell,1|\ell+\mu_{i+12},1)u_\beta(\ell,1|\ell+\mu_{i+12},1)\Big], \tag{1.74}$$

where

$$\vec{\mu}_1 = \vec{a}_1 , \vec{\mu}_2 = \vec{a}_2 , \vec{\mu}_3 = \vec{a}_3 ,$$

$$\vec{\mu}_4 = (\vec{a}_3-\vec{a}_2) , \vec{\mu}_5 = (\vec{a}_1-\vec{a}_3) , \vec{\mu}_6 = (\vec{a}_1-\vec{a}_2) ,$$

$$\vec{\mu}_7 = -\vec{\mu}_1 , \vec{\mu}_8 = -\vec{\mu}_2 , \vec{\mu}_9 = -\vec{\mu}_3 , \tag{1.75a}$$

$$\vec{\mu}_{10} = -\vec{\mu}_4 , \vec{\mu}_{11} = -\vec{\mu}_5 , \vec{\mu}_{12} = -\vec{\mu}_6 ,$$

and

$$\vec{\mu}_{i+12} = -\vec{\mu}_i \quad \text{for} \quad 1 \leq i \leq 12 . \tag{1.75b}$$

The $\vec{\mu}_i$ are the position vectors to the second nearest neighbors from the atom of interest. In this case, the $\vec{\mu}_i$ for $1 \leq i \leq 12$ are the position vectors from the origin to the twelve nearest face centered sites. Using Eqs. (1.63), (1.64) and (1.75b) we have

$$\phi_{\alpha\beta}(\ell,0|\ell+\mu_i,0) = \phi_{\alpha\beta}(0,0|\mu_i,0) , \tag{1.76a}$$

$$\phi_{\alpha\beta}(\ell,1|\ell+\mu_{i+12},1) = \phi_{\alpha\beta}(0,0|\mu_i,0) \quad . \tag{1.76b}$$

So we can write Eq. (1.74) as

$$\Phi_2^{2^\circ} = \frac{1}{4}\sum_{\ell\alpha\beta}\sum_{i=1}^{12}\phi_{\alpha\beta}(0,0|\mu_i,0)\Big[u_\alpha(\ell,0|\ell+\mu_i,0)u_\beta(\ell,0|\ell+\mu_i,0) + u_\alpha(\ell,1|\ell-\mu_i,1)u_\beta(\ell,1|\ell-\mu_i,1)\Big] \quad . \tag{1.77}$$

Noting that

$$\vec{\mu}_{i+6} = -\vec{\mu}_i \ , \ 1 \le i \le 6 \tag{1.78}$$

we obtain

$$\phi_{\alpha\beta}(0,0|\mu_{i+6},0) = \phi_{\alpha\beta}(0,0|\mu_i,0) \ , 1 \le i \le 6 \ . \tag{1.79}$$

Therefore we only need compute six matrices. Using Eq. (1.57b) one obtains

$$\overleftrightarrow{\phi}(0,0|\mu_1,0) = \begin{pmatrix} \mu & \nu & 0 \\ \nu & \mu & 0 \\ 0 & 0 & \lambda \end{pmatrix} \quad \overleftrightarrow{\phi}(0,0|\mu_2,0) = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \mu & \nu \\ 0 & \nu & \mu \end{pmatrix}$$

$$\overleftrightarrow{\phi}(0,0|\mu_3,0) = \begin{pmatrix} \mu & 0 & \nu \\ 0 & \lambda & 0 \\ \nu & 0 & \mu \end{pmatrix} \quad \overleftrightarrow{\phi}(0,0|\mu_4,0) = \begin{pmatrix} \mu & -\nu & 0 \\ -\nu & \mu & 0 \\ 0 & 0 & \lambda \end{pmatrix}$$

$$\overleftrightarrow{\phi}(0,0|\mu_5,0) = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \mu & -\nu \\ 0 & -\nu & \mu \end{pmatrix} \quad \overleftrightarrow{\phi}(0,0|\mu_6,0) = \begin{pmatrix} \mu & 0 & -\nu \\ 0 & \lambda & 0 \\ -\nu & 0 & \mu \end{pmatrix} \ . \tag{1.80}$$

Here we have defined the force constants μ,ν and λ as

$$\mu = \frac{1}{2}\left(\phi_2''(r_2) + \frac{\phi_2'(r_2)}{r_2}\right) \tag{1.81a}$$

$$\nu = \frac{1}{2}\left(\phi_2''(r_2) - \frac{\phi_2'(r_2)}{r_2}\right) \tag{1.81b}$$

$$\lambda = (\mu-\nu) = \frac{\phi_2'(r_2)}{r_2} \quad . \tag{1.81c}$$

Again, for the sake of being explicit, we have labeled the second neighbor potential function $\phi_2(r)$. The derivatives are to be evaluated at the second nearest neighbor distance Eq. (1.9b). Direct computation using Eq. (1.77) yields

$$\frac{\partial \Phi_2^{2^\circ}}{\partial u_\alpha(\ell,0)} = \sum_{i=1}^{12} \sum_{\beta} \phi_{\alpha\beta}(0,0|\mu_i,0)u_\beta(\ell,0|\ell+\mu_i,0) \tag{1.82a}$$

$$\frac{\partial \Phi_2^{2^\circ}}{\partial u_\alpha(\ell,1)} = \sum_{i=1}^{12} \sum_{\beta} \phi_{\alpha\beta}(0,0|\mu_i 0)u_\beta(\ell,1|\ell-\mu_i,1) . \tag{1.82b}$$

Using Eqs. (1.71) and (1.82) we obtain

$$D_{\alpha\beta}^{2^\circ}(0,1|\vec{k}) = 0 \tag{1.83a}$$

$$D_{\alpha\beta}^{2^\circ}(0,0|\vec{k}) = \frac{2}{M} \sum_{i=1}^{6} \phi_{\alpha\beta}(0,0|\mu_i,0)[1 - \cos(\vec{k}\cdot\vec{\mu}_i)] \ . \tag{1.83b}$$

The first equation expresses the fact that the second neighbor interaction produces no coupling between the $\kappa = 0$ and $\kappa = 1$ fcc sublattices. In obtaining the second equation we have also used Eqs. (1.78) and (1.79).

THIRD NEIGHBOR CONTRIBUTION

Evaluating the sum in Eq. (1.59) over third nearest neighbors we obtain

$$\Phi_2^{3^\circ} = \frac{1}{4} \sum_{\ell\alpha\beta} \sum_{i=1}^{12} \Big[\phi_{\alpha\beta}(\ell,0|\ell+\tau_i,1) u_\alpha(\ell,0|\ell+\tau_i,1) u_\beta(\ell,0|\ell+\tau_i,1)$$

$$+ \phi_{\alpha\beta}(\ell,1|\ell+\tau_{i+12},0) u_\alpha(\ell,1|\ell+\tau_{i+12},0) u_\beta(\ell,1|\ell+\tau_{i+12},0) \Big] \tag{1.84}$$

where

$$\vec{\tau}_1 = (\vec{a}_3 - \vec{a}_1), \; \vec{\tau}_2 = (\vec{a}_3 - \vec{a}_1 - \vec{a}_2), \; \vec{\tau}_3 = (\vec{a}_3 - \vec{a}_2),$$

$$\vec{\tau}_4 = (\vec{a}_2 - \vec{a}_1), \; \vec{\tau}_5 = (\vec{a}_2 - \vec{a}_3), \; \vec{\tau}_6 = (\vec{a}_2 - \vec{a}_1 - \vec{a}_3),$$

$$\vec{\tau}_7 = (\vec{a}_1 - \vec{a}_2 - \vec{a}_3), \; \vec{\tau}_8 = (\vec{a}_1 - \vec{a}_2), \; \vec{\tau}_9 = (\vec{a}_1 - \vec{a}_3),$$

$$\vec{\tau}_{10} = -(\vec{a}_2 + \vec{a}_3), \; \vec{\tau}_{11} = -(\vec{a}_1 + \vec{a}_3), \; \vec{\tau}_{12} = -(\vec{a}_1 + \vec{a}_2), \tag{1.85a}$$

and

$$\vec{\tau}_{i+12} = -\vec{\tau}_i \quad \text{for} \quad 1 \leq i \leq 12 \,. \tag{1.85b}$$

The $\vec{\tau}_i$ are the translation vectors to the unit cells of the third nearest neighbors from the atom of interest. Using Eqs. (1.63), (1.64) and (1.85b) we have

$$\phi_{\alpha\beta}(\ell,0|\ell+\tau_i,1) = \phi_{\alpha\beta}(0,0|\tau_i,1) \tag{1.86a}$$

$$\phi_{\alpha\beta}(\ell,1|\ell+\tau_{i+12},0) = \phi_{\alpha\beta}(0,0|\tau_i,1) \,. \tag{1.86b}$$

So we can write Eq. (1.84) as

$$\Phi_2^{3^\circ} = \frac{1}{4} \sum_{\ell\alpha\beta} \sum_{i=1}^{12} \phi_{\alpha\beta}(0,0|\tau_i,1)[u_\alpha(\ell,0|\ell+\tau_i,1)u_\beta(\ell,0|\ell+\tau_i,1)$$

$$+ u_\alpha(\ell,1|\ell-\tau_i,0)u_\beta(\ell,1|\ell-\tau_i,0)] \; . \qquad (1.87)$$

From the definition Eq. (1.57b) we compute the twelve matrices $\phi_{\alpha\beta}(0,0|\tau_i,1)$ and exhibit them explicitly

$$\overleftrightarrow{\phi}(0,0|\tau_1,1) = \begin{pmatrix} \mu' & -\nu' & \delta' \\ -\nu' & \mu' & -\delta' \\ \delta' & -\delta' & \lambda' \end{pmatrix} \qquad \overleftrightarrow{\phi}(0,0|\tau_2,1) = \begin{pmatrix} \mu' & -\delta' & \nu' \\ -\delta' & \lambda' & -\delta \\ \nu' & -\delta' & \mu' \end{pmatrix}$$

$$\overleftrightarrow{\phi}(0,0|\tau_3,1) = \begin{pmatrix} \lambda' & -\delta' & \delta' \\ -\delta' & \mu' & -\nu' \\ \delta' & -\nu' & \mu' \end{pmatrix} \qquad \overleftrightarrow{\phi}(0,0|\tau_4,1) = \begin{pmatrix} \mu' & -\nu' & -\delta' \\ -\nu' & \mu' & \delta' \\ -\delta' & \delta' & \lambda' \end{pmatrix}$$

$$\overleftrightarrow{\phi}(0,0|\tau_5,1) = \begin{pmatrix} \mu' & -\delta' & -\nu' \\ -\delta' & \lambda' & \delta' \\ -\nu' & \delta' & \mu' \end{pmatrix} \qquad \overleftrightarrow{\phi}(0,0|\tau_6,1) = \begin{pmatrix} \lambda' & -\delta' & -\delta' \\ -\delta' & \mu' & \nu' \\ -\delta' & \nu' & \mu' \end{pmatrix}$$

$$\overleftrightarrow{\phi}(0,0|\tau_7,1) = \begin{pmatrix} \mu' & \nu' & -\delta' \\ \nu' & \mu' & -\delta' \\ -\delta' & -\delta' & \lambda' \end{pmatrix} \qquad \overleftrightarrow{\phi}(0,0|\tau_8,1) = \begin{pmatrix} \lambda' & \delta' & -\delta' \\ \delta' & \mu' & -\nu' \\ -\delta' & -\nu' & \mu' \end{pmatrix}$$

$$\overleftrightarrow{\phi}(0,0|\tau_9,1) = \begin{pmatrix} \mu' & \delta' & -\nu' \\ \delta' & \lambda' & -\delta' \\ -\nu' & -\delta' & \mu' \end{pmatrix} \qquad \overleftrightarrow{\phi}(0,0|\tau_{10},1) = \begin{pmatrix} \mu' & \nu' & \delta' \\ \nu' & \mu' & \delta' \\ \delta' & \delta' & \lambda' \end{pmatrix}$$

$$\overleftrightarrow{\phi}(0,0|\tau_{11},1) = \begin{pmatrix} \lambda' & \delta' & \delta' \\ \delta' & \mu' & \nu' \\ \delta' & \nu' & \mu' \end{pmatrix} \qquad \overleftrightarrow{\phi}(0,0|\tau_{12},1) = \begin{pmatrix} \mu' & \delta' & \nu' \\ \delta' & \lambda' & \delta' \\ \nu' & \delta' & \mu' \end{pmatrix} . \tag{1.88}$$

Here we have defined the force constants $\mu',\nu',\delta',\lambda'$ as

$$\mu' = \frac{1}{11}[\phi_3''(r_3) + \frac{10}{r_3}\phi_3'(r_3)] \tag{1.89a}$$

$$\nu' = \frac{1}{11}[\phi_3''(r_3) - \frac{1}{r_3}\phi_3'(r_3)] \tag{1.89b}$$

$$\delta' = 3\nu' = \frac{3}{11}[\phi_3''(r_3) - \frac{1}{r_3}\phi_3'(r_3)] \tag{1.89c}$$

$$\lambda' = (\mu'+8\nu') = [\frac{9}{11}\phi_3''(r_3) + \frac{2}{11r_3}\phi_3'(r_3)] . \tag{1.89d}$$

Again, to be explicit, we have labeled the third neighbor potential function $\phi_3(r)$. The derivatives are to be evaluated at the third neighbor distance Eq. (1.9c).

Direct computation using Eq. (1.87) yields

$$\frac{\partial\Phi_2^{3^\circ}}{\partial u_\alpha(\ell,0)} = \sum_{i=1}^{12}\sum_\beta \phi_{\alpha\beta}(0,0|\tau_i,1)u_\beta(\ell,0|\ell+\tau_i,1) \tag{1.90a}$$

$$\frac{\partial\Phi_2^{3^\circ}}{\partial u_\alpha(\ell,1)} = \sum_{i=1}^{12}\sum_\beta \phi_{\alpha\beta}(0,0|\tau_i,1)u_\beta(\ell,1|\ell-\tau_i,0) \tag{1.90b}$$

Using Eqs. (1.71) and (1.90) we obtain

$$D_{\alpha\beta}^{3^\circ}(0,0|\vec{k}) = \frac{1}{M}\sum_{i=1}^{12}\phi_{\alpha\beta}(0,0|\tau_i,1) \tag{1.91a}$$

$$D^{3^\circ}_{\alpha\beta}(0,1|\vec{k}) = -\frac{1}{M}\sum_{i=1}^{12}\phi_{\alpha\beta}(0,0|\tau_i,1)e^{i\vec{k}\cdot\vec{\tau}_i} \quad . \qquad (1.91b) \; .$$

Addition of the matrices Eq. (1.88) gives more explicitly

$$\tilde{D}^{3^\circ}(0,0|\vec{k}) = \frac{(8\mu' + 4\lambda')}{M}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} \quad . \qquad (1.91c)$$

FOURTH NEIGHBOR CONTRIBUTION

Evaluating the sum in Eq. (1.59) over fourth nearest neighbors we obtain

$$\Phi_2^{4^\circ} = \frac{1}{4} \sum_{\ell\alpha\beta} \sum_{i=1}^{6} \Big[\phi_{\alpha\beta}(\ell,0|\ell+\lambda_i,0) u_\alpha(\ell,0|\ell+\lambda_i,0) u_\beta(\ell,0|\ell+\lambda_i,0)$$
$$+ \phi_{\alpha\beta}(\ell,1|\ell+\lambda_{i+6},1) u_\alpha(\ell,1|\ell+\lambda_{i+6},1) u_\beta(\ell,1|\ell+\lambda_{i+6},1) \Big] \tag{1.92}$$

where

$$\vec{\lambda}_1 = a\hat{e}_1 , \vec{\lambda}_2 = a\hat{e}_2 , \vec{\lambda}_3 = a\hat{e}_3$$
$$\vec{\lambda}_4 = -\vec{\lambda}_1 , \vec{\lambda}_5 = -\vec{\lambda}_2 , \vec{\lambda}_6 = -\vec{\lambda}_3 \tag{1.93a}$$
$$\vec{\lambda}_{i+6} = -\vec{\lambda}_i \quad \text{for} \quad 1 \leq i \leq 6 . \tag{1.93b}$$

The $\vec{\lambda}_i$ are the position vectors to the fourth nearest neighbors from the atom of interest. In this case, the $\vec{\lambda}_i$ for $1 \leq i \leq 6$ are the position vectors from the origin to the six nearest simple cubic lattice sites. Noting that

$$\phi_{\alpha\beta}(\ell,0|\ell+\lambda_i,0) = \phi_{\alpha\beta}(0,0|\lambda_i,) \tag{1.94a}$$
$$\phi_{\alpha\beta}(\ell,1|\ell+\lambda_{i+6},1) = \phi_{\alpha\beta}(0,0|\lambda_i,0) \tag{1.94b}$$

we can write Eq. (1.92) as

$$\Phi_2^{4^\circ} = \frac{1}{4} \sum_{\ell\alpha\beta} \sum_{i=1}^{6} \phi_{\alpha\beta}(0,0|\lambda_i,0)\Big[u_\alpha(\ell,0|\ell+\lambda_i,0)u_\beta(\ell,0|\ell+\lambda_i,0)$$
$$+ u_\alpha(\ell,1|\ell-\lambda_i,1)u_\beta(\ell,1|\ell-\lambda_i,1)\Big] \quad . \tag{1.95}$$

Since from Eqs. (1.93a), (1.63) and (1.64)

$$\phi_{\alpha\beta}(0,0|\lambda_{i+3},0) = \phi_{\alpha\beta}(0,0|\lambda_i,0) \ , \ 1 \le i \le 3 \tag{1.96}$$

we only need compute three matrices. Using Eq. (1.57b) one obtains

$$\overset{\leftrightarrow}{\phi}(0,0|\lambda_1,0) = \begin{pmatrix} \lambda'' & 0 & 0 \\ 0 & \mu'' & 0 \\ 0 & 0 & \mu'' \end{pmatrix} \qquad \overset{\leftrightarrow}{\phi}(0,0|\lambda_2,0) = \begin{pmatrix} \mu'' & 0 & 0 \\ 0 & \lambda'' & 0 \\ 0 & 0 & \mu'' \end{pmatrix}$$

$$\overset{\leftrightarrow}{\phi}(0,0|\lambda_3,0) = \begin{pmatrix} \mu'' & 0 & 0 \\ 0 & \mu'' & 0 \\ 0 & 0 & \lambda'' \end{pmatrix} . \tag{1.97}$$

Here we have defined the force constants μ'' and λ'' as

$$\mu'' = \frac{\phi_4'(a)}{a} \tag{1.98a}$$

$$\lambda'' = \phi_4''(a) \ . \tag{1.98b}$$

The fourth neighbor potential function we have labeled $\phi_4(r)$ and the derivatives are to be evaluated at the fourth neighbor distance, which is the conventional cube edge. (see Fig. 2)

One comment is appropriate at this point. Our notation for the force constants, Eqs. (1.69, 1.81, 1.89, 1.98), has been chosen to agree with the paper by Herman.[18]

Direct computation using Eq. (1.95) yields

$$\frac{\partial \Phi_2^{4^\circ}}{\partial u_\alpha(\ell,0)} = \sum_{i=1}^{6} \sum_{\beta} \phi_{\alpha\beta}(0,0|\lambda_i,0) u_\beta(\ell,0|\ell+\lambda_i,0) \qquad (1.99a)$$

$$\frac{\partial \Phi_2^{4^\circ}}{\partial u_\alpha(\ell,1)} = \sum_{i=1}^{6} \sum_{\beta} \phi_{\alpha\beta}(0,0|\lambda_i,0) u_\beta(\ell,1|\ell-\lambda_i,1) . \qquad (1.99b)$$

Using Eqs. (1.71) and (1.98) we obtain

$$D^{4^\circ}_{\alpha\beta}(0,1|\vec{k}) = 0 \qquad (1.100a)$$

$$D^{4^\circ}_{\alpha\beta}(0,0|\vec{k}) = \frac{2}{M} \sum_{i=1}^{3} \phi_{\alpha\beta}(0,0|\lambda_i,0)(1 - \cos \vec{k}\cdot\vec{\lambda}_i) . \qquad (1.100b)$$

Letting

$$\vec{k} = k_1\hat{e}_1 + k_2\hat{e}_2 + k_3\hat{e}_3 , \qquad (1.101)$$

we obtain the more explicit form

$$D^{4^\circ}_{\alpha\beta}(0,0|\vec{k}) = D^{4^\circ}_{\alpha\alpha}(0,0|\vec{k})\delta_{\alpha\beta} , \qquad (1.102)$$

with

$$D^{4^\circ}_{11}(0,0|\vec{k}) = \frac{4}{M}\left[\lambda'' \sin^2\left(\frac{k_1 a}{2}\right) + \mu'' \sin^2\left(\frac{k_2 a}{2}\right) + \mu'' \sin^2\left(\frac{k_3 a}{2}\right)\right] \qquad (1.103a)$$

$$D_{22}^{4^\circ}(0,0|\vec{k}) = \frac{4}{M}\left[\mu''\sin^2\left(\frac{k_1a}{2}\right)+\lambda''\sin^2\left(\frac{k_2a}{2}\right)+\mu''\sin^2\left(\frac{k_3a}{2}\right)\right] \tag{1.103b}$$

$$D_{33}^{4^\circ}(0,0|\vec{k}) = \frac{4}{M}\left[\mu''\sin^2\left(\frac{k_1a}{2}\right)+\mu''\sin^2 \frac{k_2a}{2} +\lambda''\sin^2\left(\frac{k_3a}{2}\right)\right]. \tag{1.103b}$$

Eq. (1.100a) expresses the fact that the fourth neighbor interaction produces no coupling between the $\kappa = 0$ and $\kappa = 1$ sublattices. In obtaining Eq. (1.100b) we have also used Eqs. (1.93a) and (1.96).

ANGLE BENDING CONTRIBUTION

The angle bending contribution to the potential energy is a three body force. The reason for this is that three points are necessary to define an angle. Because of this feature, the angle bending contribution to the dynamical matrix requires much more computational effort to obtain than the central potential contributions. For reference purposes we include a more complete discussion of angle bending in Appendix A. In this section we only outline the results found there.

We consider "pure" angle bending of the form

$$\Phi_\theta = \frac{\sigma r_o^2}{2}\sum_{\ell}\begin{bmatrix}\Delta\theta^2(\ell,0|\ell+\delta_1,1|\ell+\delta_2,1)+\Delta\theta^2(\ell,0|\ell+\delta_1,1|\ell+\delta_3,1)\\ +\Delta\theta^2(\ell,0|\ell+\delta_1,1|\ell+\delta_4,1)+\Delta\theta^2(\ell,0|\ell+\delta_2,1|\ell+\delta_3,1)\\ +\Delta\theta^2(\ell,0|\ell+\delta_2,1|\ell+\delta_4,1)+\Delta\theta^2(\ell,0|\ell+\delta_3,1|\ell+\delta_4,1)\\ +\Delta\theta^2(\ell,1|\ell+\delta_5,0|\ell+\delta_6,0)+\Delta\theta^2(\ell,1|\ell+\delta_5,0|\ell+\delta_7,0)\\ +\Delta\theta^2(\ell,1|\ell+\delta_5,0|\ell+\delta_8,0)+\Delta\theta^2(\ell,1|\ell+\delta_6,0|\ell+\delta_7,0)\\ +\Delta\theta^2(\ell,1|\ell+\delta_6,0|\ell+\delta_8,0)+\Delta\theta^2(\ell,1|\ell+\delta_7,0|\ell+\delta_8,0)\end{bmatrix} \qquad (1.104)$$

The δ_i are given by Eqs. (1.62). Here we have defined $\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'')$ as the change in angle between the atoms $(\ell\kappa)$, $(\ell'\kappa')$ and $(\ell''\kappa'')$, having $(\ell\kappa)$ at the vertex, produced by the respective lattice displacements. (see Fig. 5) The form of Eq. (1.104) is appropriate to "nearest

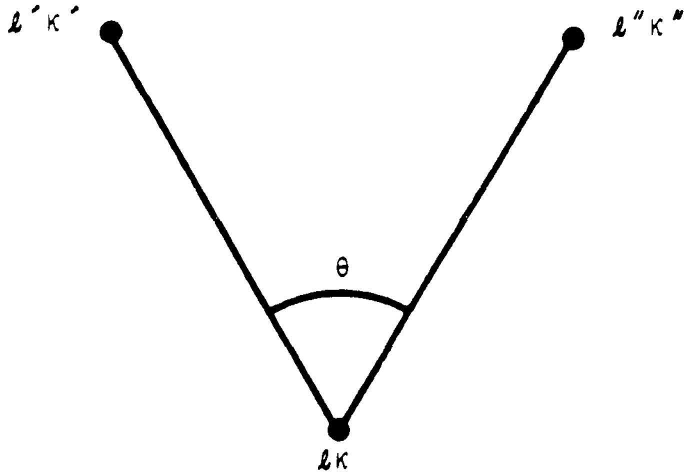


Figure 5. The angle $\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'')$ between any three atoms in the crystal. Atom $(\ell\kappa)$ is at the vertex of the angle.

neighbor" angle bending. There are six tetrahedral angles per atom and two atoms per unit cell, thus twelve terms per unit cell.

At this point we would like to make a few comments. There is some confusion in the literature concerning what is meant by nearest neighbor noncentral force. As we will see, our "nearest neighbor" angle bending potential will couple atoms that are first neighbors as well as atoms that are second neighbors, so in this sense it is not a purely nearest neighbor interaction. This point was noted by Herman.[19] However there is a difference between central potentials and what are termed central forces. We may see this by considering the force on an atom of type $\kappa = 0$ produced by a variational displacement of its nearest neighbor in the same unit cell, all other displacements being zero. We have from Eq. (1.72a)

$$F_\alpha^{1^\circ}(\ell,0) = -\frac{\partial \Phi_2^{1^\circ}}{\partial u_\alpha(\ell,0)} = \sum_\beta \phi_{\alpha\beta}(0,0|0,1)u_\beta(\ell,1) \ . \qquad (1.105)$$

The line joining the center of the two atoms is

$$\vec{R}(1) = \frac{a}{4}(\hat{e}_1 + \hat{e}_2 + \hat{e}_3) \ , \qquad (1.106)$$

and a displacement parallel to the line of centers is

$$\vec{u}(\ell,1) = u_{\parallel}(\hat{e}_1 + \hat{e}_2 + \hat{e}_3) \ . \qquad (1.107)$$

This displacement produces the force

$$\vec{F}^{1^\circ}(\ell,0) = (\alpha + 2\beta)u_{\parallel}(\hat{e}_1 + \hat{e}_2 + \hat{e}_3) \qquad (1.108a)$$

or

$$\vec{F}^{1^\circ}(\ell,0) = \phi_1''(r_0)u_{\parallel}(\hat{e}_1 + \hat{e}_2 + \hat{e}_3) \ , \qquad (1.108b)$$

where we have used Eqs. (1.68) and (1.69).

A displacement perpendicular to the line of centers is

$$\vec{u}(\ell,1) = u_{\perp}(\hat{e}_2 - \hat{e}_3) \ , \qquad (1.109)$$

as can be easily seen since

$$u_{\perp}(\hat{e}_2 - \hat{e}_3)\cdot\vec{R}(1) = 0 \ . \qquad (1.110)$$

For this displacement we obtain

$$\vec{F}^{1^\circ}(\ell,0) = (\alpha-\beta)u_{\perp}(\hat{e}_2 - \hat{e}_3) \ , \qquad (1.111a)$$

or

$$\vec{F}^{1^\circ}(\ell,0) = \frac{\phi_1'(r_0)}{r_0}\, u_{\perp}(\hat{e}_2 - \hat{e}_3) \ , \qquad (1.111b)$$

where again we have used Eqs. (1.68) and (1.69). For a "central" force, a displacement perpendicular to the line of centers of two atoms must produce no force. For the central potential to be a "central" force, we see from Eq. (1.111a) that this requires $\alpha = \beta$. This agrees with the form of the matrices Eq. (1.68) exhibited by Herman[20] for the case of central forces. If $\phi_1'(r_0) \neq 0$ we see from Eq. (1.111b) that the central potential can produce a noncentral force. If only nearest neighbor central potential interactions were present, the condition of minimum potential energy would require $\phi_1'(r_0) = 0$, but in this case the lattice is unstable, as we will see later. If in addition second neighbor central potential interactions are present, the condition of minimum potential energy does not require $\phi_1'(r_0) = 0$. Provided $\phi_1'(r_0)$ is not zero, we have an example of a first neighbor noncentral force. The somewhat misleading statement has been made by Keating[21] that, "there are no noncentral purely first-neighbor interactions present in any nonmetallic crystal." Concerning this Ludwig[22] has commented, "this is obviously not correct." We also note at this point that the noncentral force used by Keating is not "pure" angle bending. His noncentral coefficient β enters into the expression for the bulk modulus, whereas "pure" angle bending does not contribute to the bulk modulus. This is so because an isotropic homogeneous deformation leaves all angles in the crystal unchanged, and therefore any potential energy which only involves changes in angles will be zero under this type of deformation. The potential used here, Eq. (1.104), is an example of "pure" angle bending.

Now to be more precise

$$\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') - \theta^{(o)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') \ , \tag{1.112}$$

where

$$\cos\,\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \frac{\vec{x}(\ell\kappa|\ell'\kappa')\cdot\vec{x}(\ell\kappa|\ell''\kappa'')}{|\vec{x}(\ell\kappa|\ell'\kappa')||\vec{x}(\ell\kappa|\ell''\kappa'')|} \ , \tag{1.113}$$

and

$$\vec{x}(\ell\kappa|\ell'\kappa') = \vec{x}(\ell\kappa) - \vec{x}(\ell'\kappa') \tag{1.114a}$$

$$\vec{x}(\ell\kappa) = \vec{R}(\ell\kappa) + \vec{u}(\ell\kappa) \ . \tag{1.114b}$$

Here $|\vec{x}|$ denotes the magnitude of the vector $\vec{x}$. The equilibrium angles are given by Eq. (1.113) when all atoms are in the rest positions

$$\cos\,\theta^{(o)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \frac{\vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{R}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|} \ . \tag{1.115}$$

Note the symmetry property which follows from Eq. (1.113)

$$\cos\,\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \cos\,\theta(\ell\kappa|\ell''\kappa''|\ell'\kappa') \ . \tag{1.116}$$

From Eqs. (1.112-1.115) it is clear that in general $\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'')$ is a nonlinear function of the displacements $u_\alpha(\ell\kappa)$. Thus our potential Eq. (1.104) contains anaharmonic terms. Provided that $|\vec{u}(\ell\kappa|\ell'\kappa'| \div |\vec{R}(\ell\kappa|\ell'\kappa')|$ is small compared to one, we can obtain an expression for the change in angle, correct to first order in the displacements

$$\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \sum_{\alpha} \eta_{\alpha}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')u_{\alpha}(\ell\kappa|\ell'\kappa') + \sum_{\alpha} \eta_{\alpha}(\ell\kappa|\ell''\kappa''|\ell'\kappa')u_{\alpha}(\ell\kappa|\ell''\kappa'') , \tag{1.117}$$

where we have defined

$$\eta_{\alpha}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \left[\frac{\cot\,\theta^{(o)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_{\alpha}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|^{2}} - \frac{\csc\,\theta^{(o)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_{\alpha}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|}\right] . \tag{1.118}$$

From the form of Eq. (1.117) we see that the angle change depends on the difference of displacements of atoms from the vertex atom.

Direct computation using Eq. (1.115) gives

$$\cos\,\theta^{(o)} = -\,1/3 \tag{1.119a}$$

with

$$\theta^{(o)} = \theta^{(o)}(\ell,0|\ell+\delta_{1},1|\ell+\delta_{2},1) = 109.47122^{\circ} . \tag{1.119b}$$

This angle is the tetrahedral angle and is the same for each of the twelve terms in Eq. (1.104). As an example, using

Eq. (1.117) we find

$$\Delta\theta(\ell,0|\ell+\delta_1,1|\ell+\delta_2,1) = \frac{1}{\sqrt{6}\,r_o}\sum_\alpha\Big[(-\delta_{\alpha 1}-\delta_{\alpha 2}+2\delta_{\alpha 3})u_\alpha(\ell,0|\ell+\delta_1,1) + (\delta_{\alpha 1}+\delta_{\alpha 2}+2\delta_{\alpha 3})u_\alpha(\ell,0|\ell+\delta_2,1)\Big] \tag{1.120}$$

so that

$$\frac{\partial}{\partial u_\alpha(\ell,0)}\left[\frac{\sigma r_o^2}{2}\sum_{\ell'}\Delta\theta^2(\ell',0|\ell'+\delta_1,1|\ell'+\delta_2,1)\right] = \frac{2\sigma}{3}\sum_\beta\delta_{\alpha 3}\Big[(-\delta_{\beta 1}-\delta_{\beta 2}+2\delta_{\beta 3})u_\beta(\ell,0|\ell+\delta_1,1) + (\delta_{\beta 1}+\delta_{\beta 2}+2\delta_{\beta 3})u_\beta(\ell,0|\ell+\delta_2,1)\Big] . \tag{1.121}$$

This term only couples nearest neighbors. The first six terms in Eq. (1.104) are of this type. However the second six terms in Eq. (1.104) are different when differentiated as above. Consider

$$\Delta\theta(\ell,1|\ell+\delta_5,0|\ell+\ell_6,) = \frac{1}{\sqrt{6}\,r_o}\sum_\alpha\Big[(-\delta_{\alpha 1}-\delta_{\alpha 2}+2\delta_{\alpha 3})u_\alpha(\ell,1|\delta+\delta_5,0) + (\delta_{\alpha 1}+\delta_{\alpha 2}+2\delta_{\alpha 3})u_\alpha(\ell,1|\ell+\ell_6,0)\Big], \tag{1.122}$$

which gives upon differentiation

$$\frac{\partial}{\partial u_\alpha(\ell,0)}\left[\frac{\sigma r_o^2}{2}\sum_{\ell'}\Delta\theta^2(\ell,1|\ell+\delta_5,0|\ell+{}_6,1)\right] =$$

$$= \frac{\sigma}{6}\sum_\beta(-\delta_{\alpha 1}-\delta_{\alpha 2}+2\delta_{\alpha 3})\left[\begin{array}{l}(-\delta_{\beta 1}-\delta_{\beta 2}+2\delta_{\beta 3})u_\beta(\ell,0|\ell-\delta_5,1)\\ +(\delta_{\beta 1}+\delta_{\beta 2}+2\delta_{\beta 3})u_\beta(\ell-\delta_5+\delta_6,0|\ell-\delta_5,1)\end{array}\right]$$

$$+ \frac{\sigma}{6}\sum_\beta(\delta_{\alpha 1}+\delta_{\alpha 2}+2\delta_{\alpha 3})\left[\begin{array}{l}(\delta_{\beta 1}+\delta_{\beta 2}+2\delta_{\beta 3})u_\beta(\ell,0|\ell-\delta_6,1)\\ +(-\delta_{\beta 1}-\delta_{\beta 2}+2\delta_{\beta 3})u_\beta(\ell-\delta_6+\delta_5,0|\ell-\delta_6,1)\end{array}\right]. \tag{1.123}$$

This type of term couples atoms that are second neighbors as well as atoms that are first neighbors, (i.e., the atom at $\vec{R}(\ell-\delta_6+\delta_5,0)$ is a second neighbor to the atom at $\vec{R}(\ell,0)$, and similarly for $\vec{R}(\ell-\delta_5+\delta_6,0)$.) Therefore we see explicitly how the "nearest neighbor" angle bending potential couples atoms that are first neighbors as well as atoms that are second neighbors.

By successive evaluation of each term in Eq. (1.104) using Eqs. (1.117-1.118) and then differentiation of each term, applying Eq. (1.71) we can obtain the angle bending contribution to the dynamical matrix. This is a tedious exercise so we present the results here for reference purposes.

$$D_{11}^{(\theta)}(0,0|\vec{k}) = \left[\begin{aligned} &\frac{28\sigma}{3M} - \frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_2 + \frac{4\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_3 \\ &- \frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_4 - \frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_3) \\ &+ \frac{4\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_4) - \frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_3-\vec{\delta}_4) \end{aligned}\right] \tag{1.124a}$$

$$D_{12}^{(\theta)}(0,0|\vec{k}) = \left[\begin{aligned} &- \frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_2 + \frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_3-\vec{\delta}_4) \\ &- \frac{2i\sigma}{3M}\sin\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_3) + \frac{2i\sigma}{3M}\sin\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_4) \\ &- \frac{2i\sigma}{3M}\sin\vec{k}\cdot\vec{\delta}_3 + \frac{2i\sigma}{3M}\sin\vec{k}\cdot\vec{\delta}_4 \end{aligned}\right] \tag{1.124b}$$

$$D_{13}^{(\theta)}(0,0|\vec{k}) = \left[\begin{aligned} &- \frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_4 + \frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_3) \\ &+ \frac{2i\sigma}{3M}\sin\vec{k}\cdot\vec{\delta}_2 - \frac{2i\sigma}{3M}\sin\vec{k}\cdot\vec{\delta}_3 \\ &+ \frac{2i\sigma}{3M}\sin\vec{k}\cdot(\vec{\delta}_3-\vec{\delta}_4) - \frac{2i\sigma}{3M}\sin\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_4) \end{aligned}\right] \tag{1.124c}$$

$$D_{21}^{(\theta)}(0,0|\vec{k}) = D_{12}^{(\theta)^{*}}(0,0|\vec{k}) \tag{1.124d}$$

$$D_{22}^{(\theta)}(0,0|\vec{k}) = \left[\begin{aligned} &\frac{28\sigma}{3M} - \frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_2 - \frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_3 \\ &+ \frac{4\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_4 + \frac{4\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_3) \\ &- \frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_4) - \frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_3-\vec{\delta}_4) \end{aligned}\right] \tag{1.124e}$$

$$D_{23}^{(\theta)}(0,0|\vec{k}) = \left[\begin{array}{l} -\frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_3 + \frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_4) \\ -\frac{2i\sigma}{3M}\sin\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_3) - \frac{2i\sigma}{3M}\sin\vec{k}\cdot(\vec{\delta}_3-\vec{\delta}_4) \\ +\frac{2i\sigma}{3M}\sin\vec{k}\cdot\vec{\delta}_2 - \frac{2i\sigma}{3M}\sin\vec{k}\cdot\vec{\delta}_4 \end{array}\right] \tag{1.124f}$$

$$D_{31}^{(\theta)}(0,0|\vec{k}) = D_{13}^{(\theta)^*}(0,0|\vec{k}) \tag{1.124g}$$

$$D_{32}^{(\theta)}(0,0|\vec{k}) = D_{23}^{(\theta)^*}(0,0|\vec{k}) \tag{1.124h}$$

$$D_{33}^{(\theta)}(0,0|\vec{k}) = \left[\begin{array}{l} \frac{28\sigma}{3M} + \frac{4\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_2 - \frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_3 \\ -\frac{\sigma}{3M}\cos\vec{k}\cdot\vec{\delta}_4 - \frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_3) \\ -\frac{\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_2-\vec{\delta}_4) + \frac{4\sigma}{3M}\cos\vec{k}\cdot(\vec{\delta}_3-\vec{\delta}_4) \end{array}\right] . \tag{1.124i}$$

Eqs. (1.124d,g,h) were computed explicitly as a check on the algebra. They are also a consequence of the Hermitian property of the dynamical matrix Eq. (1.42a), which must be obeyed for each contribution to the dynamical matrix.

Similarly we have

$$D_{11}^{(\theta)}(0,1|\vec{k}) = -\frac{8\sigma}{3M}(1 + e^{i\vec{k}\cdot\vec{\delta}_2} + e^{i\vec{k}\cdot\vec{\delta}_3} + e^{i\vec{k}\cdot\vec{\delta}_4}) , \tag{1.125a}$$

$$D_{12}^{(\theta)}(0,1|\vec{k}) = \frac{4\sigma}{3M}(1 + e^{i\vec{k}\cdot\vec{\delta}_2} - e^{i\vec{k}\cdot\vec{\delta}_3} - e^{i\vec{k}\cdot\vec{\delta}_4}) , \tag{1.125b}$$

$$D_{13}^{(\theta)}(0,1|\vec{k}) = \frac{4\sigma}{3M}(1 - e^{i\vec{k}\cdot\vec{\delta}_2} - e^{i\vec{k}\cdot\vec{\delta}_3} + e^{i\vec{k}\cdot\vec{\delta}_4}) \qquad (1.125c)$$

$$D_{21}^{(\theta)}(0,1|\vec{k}) = D_{12}^{(\theta)}(0,1|\vec{k}) \qquad (1.125d)$$

$$D_{22}^{(\theta)}(0,1|\vec{k}) = D_{11}^{(\theta)}(0,1|\vec{k}) \qquad (1.125e)$$

$$D_{23}^{(\theta)}(0,1|\vec{k}) = \frac{4\sigma}{3M}(1 - e^{i\vec{k}\cdot\vec{\delta}_2} + e^{i\vec{k}\cdot\vec{\delta}_3} - e^{i\vec{k}\cdot\vec{\delta}_4}) \qquad (1.125f)$$

$$D_{31}^{(\theta)}(0,1|\vec{k}) = D_{13}^{(\theta)}(0,1|\vec{k}) \qquad (1.125g)$$

$$D_{32}^{(\theta)}(0,1|\vec{k}) = D_{23}^{(\theta)}(0,1|\vec{k}) \qquad (1.125h)$$

$$D_{33}^{(\theta)}(0,1|\vec{k}) = D_{11}^{(\theta)}(0,1|\vec{k}) \ . \qquad (1.125i)$$

Again, Eqs. (1.125d,g,h) were computed explicitly as a check on the algebra, they are also a consequence of Eq. (1.48), which must be satisfied for each contribution to the dynamical matrix. The $\vec{\delta}_i$ in Eqs. (1.125-1.126) are given by Eq. (1.62a). Note also that our parameter σ is 6Q in the notation of Herman.[23]

LONG-RANGE CONTRIBUTION TO THE DYNAMICAL MATRIX

The possibility of comparatively long-range forces in diamond structure crystals has an interesting history. The first lattice dynamical investigation of the diamond structure was by Max Born.[24] He considered the most general nearest neighbor interactions consistent with symmetry. The results for the elastic constants and Raman frequency in this model are

$$C_{11} = \frac{\alpha}{a} \qquad C_{12} = \frac{(2\beta-\alpha)}{a}$$

$$C_{44} = \frac{(\alpha-\beta^2/\alpha)}{a} \qquad \omega_{RA}^2 = \frac{8\alpha}{M} \quad . \tag{1.126}$$

Here α and β are the two nearest neighbor force constants. Since there are only two parameters in this model, this leads to a relation between the elastic constants known as the Born identity

$$\frac{4C_{11}(C_{11}-C_{44})}{(C_{11}+C_{12})^2} = 1 \ , \tag{1.127}$$

and also the Raman frequency

$$\omega_{RA} = \left(\frac{8aC_{11}}{M}\right)^{\frac{1}{2}} \quad . \tag{1.128}$$

When the first measurements of the elastic constants for diamond become available, Born[25] evaluated the left-hand side of Eq. (1.127) and obtained the value 1.10 instead of 1. This seemed rather good agreement, yet the ten per cent discrepancy caused Born to question whether second neighbor forces could improve matters. As it turned out, the value of 1.10 was fortuitous since later more careful measurements[26] showed the early value of C_{12} to be more than a factor of three too large, the values of C_{11} and C_{44} also had large errors. Using the experimental values[27] for diamond, silicon and germanium, we evaluate Eqs. (1.127) and (1.128) and compare to experiment in Table 1.

TABLE 1.

Comparison of Born identity Eq. (1.127) and Raman frequency Eq. (1.128) with experiment. Frequencies in radians/sec.

Crystal	$\frac{4C_{11}(C_{11}-C_{44})}{(C_{11}+C_{12})^2}$	$\left(\frac{8aC_{11}}{M}\right)^{\frac{1}{2}}$	ω_{RA}(expt.)
Diamond	1.49	3.92×10^{14}	2.51×10^{14}
Silicon	1.09	1.24×10^{14}	9.79×10^{13}
Germanium	0.995	6.95×10^{13}	5.66×10^{13}

As can be seen from Table 1, the agreement with experiment is the worst for diamond and the best for germanium. This shows the inadequacy of the nearest neighbor model to account for even the long wavelength vibrations of the crystal, though the agreement for silicon and germanium is respectable considering the simplicity of the model.

Helen Smith,[28] collaborating with Born, worked out the theory for the case of first and second neighbor interactions. Her second neighbor force constant matrices are not the most general allowed by symmetry[29] and neglect the antisymmetric second neighbor force constant. Using a three parameter version of the model developed by Smith, Hsieh[30] fit the three elastic constants of silicon and germanium and computed the specific heat of these crystals. Hsieh found that the calculated specific heat values were well below the experimental values, even at temperatures as low as 60K, the discrepancy increasing with increasing temperature. This was an indication that the normal mode frequencies in the rest of the Brillouin zone were considerably smaller than those expected from the first and second neighbor model.

When phonon dispersion curves became available from neutron scattering studies, detailed comparison between lattice model predictions and experiment was possible for short wavelength modes. Herman[31] presented an analysis of diamond structure crystals using general forces between first through sixth neighbors. He showed that it was necessary to include interactions to at least fifth neighbors in order to fit the three elastic constants, the Raman frequency and the LA and TA frequencies at the [111] zone boundary of germanium.

In attempts to reduce the number of parameters required to fit the phonon dispersion curve data, several lattice dynamical models have been introduced. Lax[32] included displacement induced quadrupole-quadrupole interactions between atoms. This was an attempt to include long range interactions within the adiabatic approximation. The shell model[33] also includes long-range electrostatic interactions, but introduces electron coordinates which are then eliminated adiabatically. The bond-charge model[34] is similar to the shell model but employs point charges between the ions that are allowed to move adiabatically. Finally there are the valence force models[35] which describe the forces between atoms in terms of bond stretching, bond angle bending and combinations of the two.

In each of the above models it was found necessary to include interactions of some type to at least fifth neighbors in order to fit the phonon dispersion curves and the elastic constants. Each of the models has attendant strengths and weaknesses. Since the author wanted a harmonic model to use for computing anharmonic properties, none of the above models were considered satisfactory for this purpose. Therefore we have investigated a model suggested by the work of Lax,[36] but with very different consequences than his quadrupole model.

NONLOCAL DIPOLE MODEL

The presence of a lattice displacement can distort the electron charge density in the vicinity of a displaced ion. This induced charge density can then interact electrostatically with a charge distortion produced by another displaced atom, giving rise to long-range interactions. How important this effect is should intuitively depend on how big a charge distortion is induced by a given lattice displacement, and how effectively this charge distortion is screened.

To put this concept on a firmer foundation, in Figure 6 is plotted the valence charge density of diamond and silicon, as computed ab initio from the electronic theory of solids.[37] This is for the lattice with all atoms in the rest positions. In Figure 7 is the induced charge density for silicon due to the presence of a [100] transverse zone boundary phonon. The induced charge density is the difference in charge densities between the distorted and undistorted lattices. Note that there is a striking dipole contribution to the induced charge density, as well as contributions from higher multipoles. Since we only want to model the longest range contribution to the forces, we will examine the dipole contribution to the induced charge density in detail.

We begin by writing the dipole moment induced about atom $(\ell\kappa)$ due to lattice displacements as

Figure 6. Valence charge density for diamond and silicon. Units are (e/Ω_o) . (Courtesy M.T. Yin, Ref. 37)

Valence charge density (110 plane)

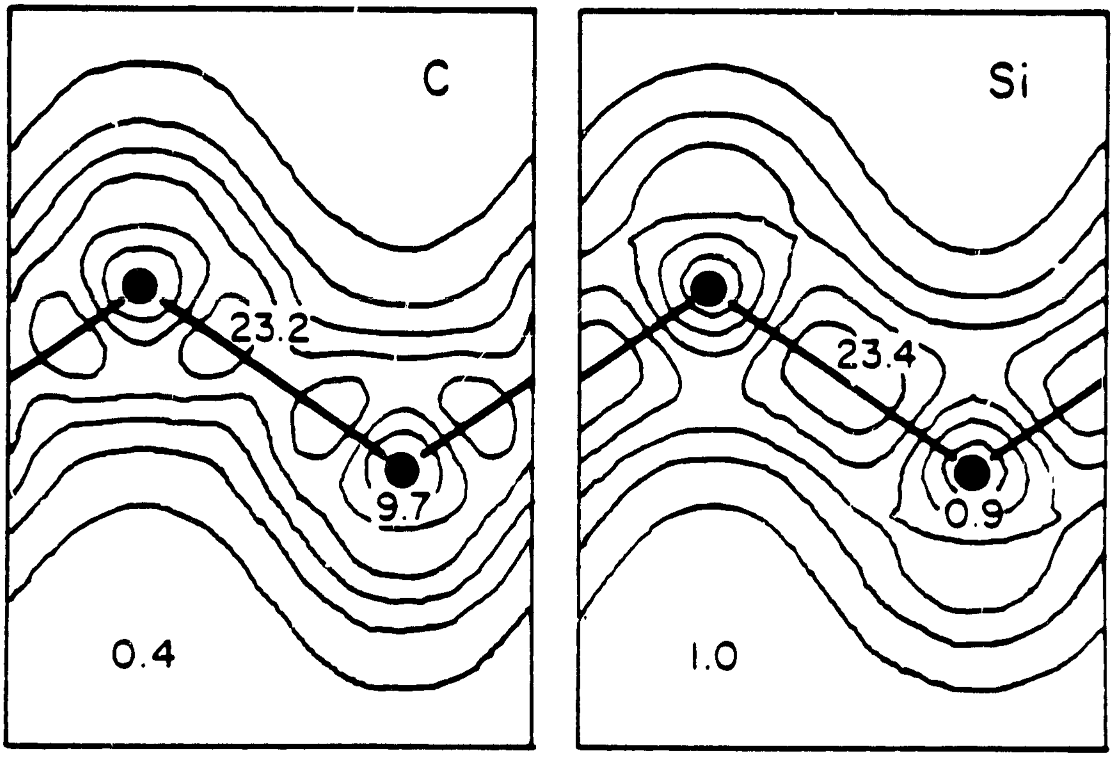
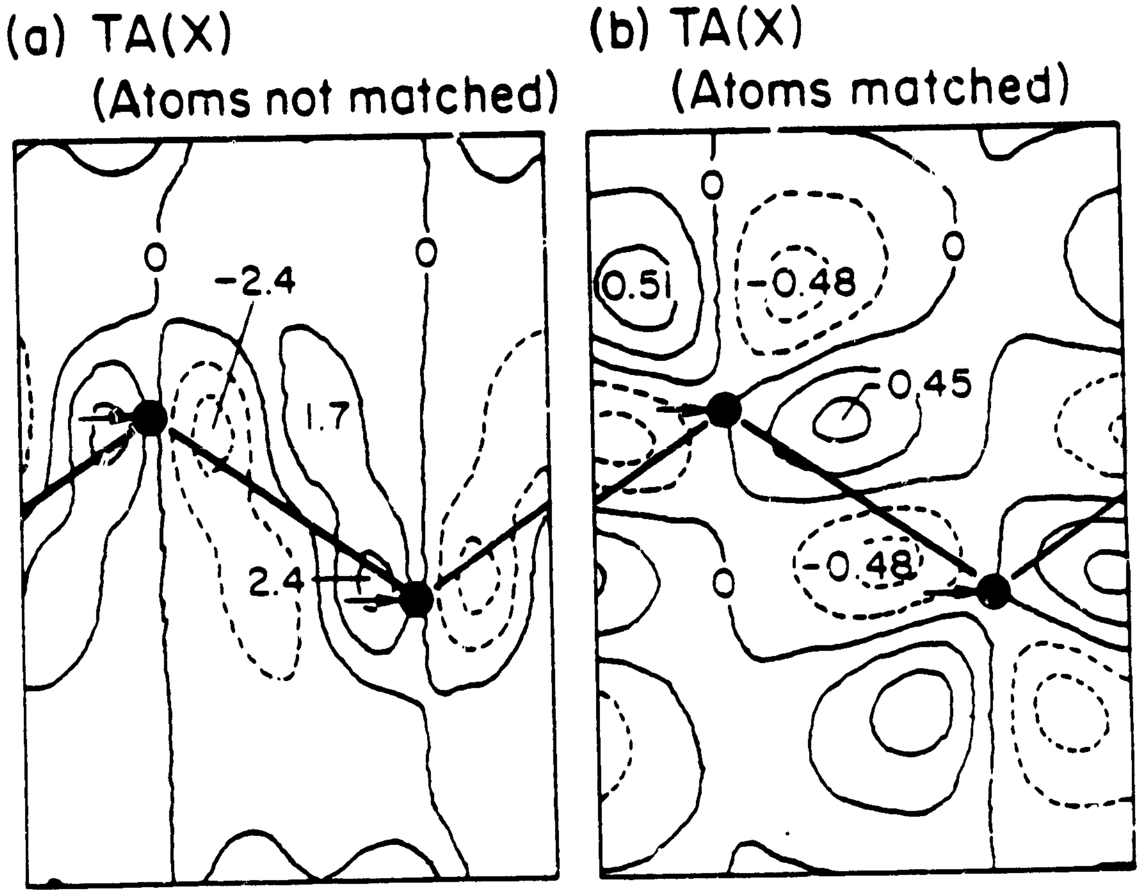


Figure 7. [110] plane charge density induced in silicon by the presence of a TAX phonon. Units are (e/Ω_o). Amplitude of the phonon is .077Å . Atoms not matched corresponds to taking the difference in charge densities with and without the phonon using the same origin of coordinates. Atoms matched corresponds to taking the difference in charge densities with the origin of coordinates for the phonon present charge density shifted so that the atoms shown are in the original undistorted positions. (Courtesy M.T. Yin, Ref. 37)


(a) TA(X)
(Atoms not matched)
0
0
-2.4
1.7
2.4
(b) TA(X)
(Atoms matched)
0
0
0.51
-0.48
0.45
0
-0.48

$$p_\alpha(\ell\kappa) = \sum_{\ell'\kappa'\beta} p_{\alpha\beta}(\ell\kappa|\ell'\kappa')u_\beta(\ell'\kappa') \ . \qquad (1.129)$$

This form has been mentioned by Lax[38] to justify his quadrupole model. Although the form of Eq. (1.129) is similar to the work of Minnick,[39] our interaction energy is not the same as his and leads to rather different consequences. Since Eq. (1.129) had not been applied to the diamond structure in the manner that we apply it, it was not known what effect it would have on the phonon spectrum. Therefore we have not considered polarizability effects, which in our approach requires considerable additional effort to include.

The total dipole moment of the crystal may be written as

$$P_\alpha = \sum_{\ell\kappa} p_\alpha(\ell\kappa) \ , \qquad (1.130)$$

so that

$$P_\alpha = \sum_{\ell\kappa} \sum_{\ell'\kappa'\beta} p_{\alpha\beta}(\ell\kappa|\ell'\kappa')u_\beta(\ell'\kappa') \ . \qquad (1.131)$$

Defining

$$M_{\alpha\beta}(\ell'\kappa') = \sum_{\ell\kappa} p_{\alpha\beta}(\ell\kappa|\ell'\kappa') \ , \qquad (1.132)$$

we have

$$P_\alpha = \sum_{\ell'\kappa'\beta} M_{\alpha\beta}(\ell'\kappa')u_\beta(\ell'\kappa') \ . \qquad (1.133)$$

The transformation property of the total electric moment under the operation $\{S|\vec{v}(s)+\vec{R}(m)\}$ (see Eq. (1.34)) leads to[40]

$$M_{\mu\nu}(LK) = \sum_{\alpha\beta} S_{\mu\alpha} S_{\nu\beta} M_{\alpha\beta}(\ell\kappa) \ . \qquad (1.134)$$

The special case of a pure lattice translation by $\vec{R}(m)$ gives

$$M_{\mu\nu}(\ell+m,\kappa) = M_{\mu\nu}(\ell,\kappa) = M_{\mu\nu}(0,\kappa) \ , \qquad (1.135)$$

so that $M_{\mu\nu}(\ell\kappa)$ does not depend on the unit cell index. Since an arbitrary uniform translation of the crystal as a whole must not change the total dipole moment, we obtain the requirement that

$$\sum_{\ell'\kappa'} M_{\alpha\beta}(\ell'\kappa') = 0 \ . \qquad (1.136)$$

Using Eqs. (1.135) and (1.136) we also have

$$\sum_{\kappa} M_{\alpha\beta}(0,\kappa) = 0 \ . \qquad (1.137)$$

This is the statement that the primitive unit cell is neutral if $M_{\alpha\beta}(0,\kappa)$ is thought of as some type of effective charge. Applying the inversion operation Eq. (1.36) yields

$$M_{\alpha\beta}(\ell,0) = M_{\alpha\beta}(-\ell,1) \ . \qquad (1.138)$$

With the addition of lattice translation invariance, Eq. (1.135), we obtain

$$M_{\alpha\beta}(0,0) = M_{\alpha\beta}(0,1) \ , \tag{1.139}$$

so that Eq. (1.137) becomes

$$M_{\alpha\beta}(0,0) = 0 \ , \tag{1.140a}$$

or

$$M_{\alpha\beta}(\ell,\kappa) = 0 \ . \tag{1.140b}$$

Eq. (1.140b) expresses the fact that no linear term in the total electric moment exsists in diamond structure crystals. This has the consequence that the infrared absorption spectrum must be explained by two and higher phonon processes,[41] although the presence of impurities and surfaces can break the translation invariance and allow a first order moment to exsist.

From Eqs. (1.140) and (1.132) we obtain for diamond structure the requirement that

$$\sum_{\ell\kappa} p_{\alpha\beta}(\ell\kappa|\ell'\kappa') = 0 \ . \tag{1.141}$$

Note that Eq. (1.141) does not require that $p_{\alpha}(\ell\kappa)$ be zero in the bulk crystal. This would only result if we had used a strictly local form for $p_{\alpha\beta}(\ell\kappa|\ell'\kappa')$, as used in the work of Trullinger.[42]

The transformation property of the dipole moment $p_\alpha(\ell\kappa)$ under the operation $\{S|\vec{v}(S)+\vec{R}(m)\}$ leads to[43]

$$p_{\mu\nu}(LK|L'K') = \sum_{\alpha\beta} S_{\mu\alpha}S_{\nu\beta}p_{\alpha\beta}(\ell\kappa|\ell'\kappa') \ . \tag{1.142}$$

The special case of a pure lattice translation by $\vec{R}(m)$ gives

$$p_{\alpha\beta}(\ell+m,\kappa|\ell'+m,\kappa') = p_{\alpha\beta}(\ell\kappa|\ell'\kappa') \ , \tag{1.143}$$

so that in particular

$$p_{\alpha\beta}(\ell\kappa|\ell'\kappa') = p_{\alpha\beta}(0,\kappa|\ell'-\ell,\kappa') = p_{\alpha\beta}(\ell-\ell',\kappa|0,\kappa') \ . \tag{1.144}$$

Thus we see that the moment coefficients transform in the same manner as the second order force constants Eq. (1.35). However, the moment coefficients $p_{\alpha\beta}(\ell\kappa|\ell'\kappa')$ need not obey the "flip" symmetry property Eq. (1.26) that is obeyed by the second order force constants.

Consider now the moment coefficients appropriate to the case of nearest neighbor nonlocality. This is the simplest type of nonlocality and is the model we will investigate. Applying Eq. (1.129) to this case we have

$$p_\alpha(\ell,0) = \sum_\beta p_{\alpha\beta}(\ell,0|\ell,0)u_\beta(\ell,0)$$
$$+ \sum_\beta \sum_{i=1}^{4} p_{\alpha\beta}(\ell,0|\ell+\delta_i,1)u_\beta(\ell+\delta_i,1) \tag{1.145a}$$

$$p_\alpha(\ell,1) = \sum_\beta p_{\alpha\beta}(\ell,1|\ell,1)u_\beta(\ell,1)$$

$$+ \sum_\beta \sum_{i=4}^{8} p_{\alpha\beta}(\ell,1|\ell+\delta_i,0)u_\beta(\ell+\delta_i,0) \, , \qquad (1.145b)$$

where the δ_i are given by Eqs. (1.62). Translation invariance plus inversion symmetry analogous to Eqs. (1.40) yields

$$p_{\beta\alpha}(\ell,0|\ell,0) = p_{\alpha\beta}(0,0|0,0) = p_{\alpha\beta}(\ell,1|\ell,1) \qquad (1.146a)$$

and

$$p_{\alpha\beta}(\ell,1|\ell+\delta_i,0) = p_{\alpha\beta}(0,0|-\delta_i,1) \, . \qquad (1.146b)$$

Using Eqs. (1.146) and (1.62b) we obtain

$$p_\alpha(\ell,0) = \sum_\beta p_{\alpha\beta}(0,0|0,0)u_\beta(\ell,0)$$

$$+ \sum_\beta \sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1)u_\beta(\ell+\delta_i,1) \qquad (1.147a)$$

$$p_\alpha(\ell,1) = \sum_\beta p_{\alpha\beta}(0,0|0,0)u_\beta(\ell,1)$$

$$+ \sum_\beta \sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1)u_\beta(\ell-\delta_i,0) \, . \qquad (1.147b)$$

Applying the requirement Eq. (1.141) and inversion symmetry analogous to Eq. (1.40c) yields

$$p_{\alpha\beta}(0,0|0,0) = - \sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1) \, , \qquad (1.148)$$

so that

$$p_\alpha(\ell,0) = \sum_\beta \sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1)(u_\beta(\ell+\delta_i,1)-u_\beta(\ell,0)) \tag{1.149a}$$

$$p_\alpha(\ell,1) = \sum_\beta \sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1)(u_\beta(\ell-\delta_i,0)-u_\beta(\ell,1)) \; . \tag{1.149b}$$

Using Eqs. (1.142) and (1.68), we can immediately write down the four matrices

$$\overleftrightarrow{p}(0,0|\delta_1,1) = \begin{pmatrix} p_1 & p_2 & p_2 \\ p_2 & p_1 & p_2 \\ p_2 & p_2 & p_1 \end{pmatrix} \quad \overleftrightarrow{p}(0,0|\delta_2,1) = \begin{pmatrix} p_1 & p_2 & -p_2 \\ p_2 & p_1 & -p_2 \\ -p_2 & -p_2 & p_1 \end{pmatrix}$$

$$\overleftrightarrow{p}(0,0|\delta_3,1) = \begin{pmatrix} p_1 & -p_2 & -p_2 \\ -p_2 & p_1 & p_2 \\ -p_2 & p_2 & p_1 \end{pmatrix} \quad \overleftrightarrow{p}(0,0|\delta_4,1) = \begin{pmatrix} p_1 & -p_2 & p_2 \\ -p_2 & p_1 & -p_2 \\ p_2 & -p_2 & p_1 \end{pmatrix} . \tag{1.150}$$

Here p_1 and p_2 are parameters to be determined and have the dimensions of charge. The matrices Eq. (1.150) agree with those of Lax.[44] Using the explicit form of the matrices we obtain

$$\sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1) = 4p_1\delta_{\alpha\beta} \; , \tag{1.151a}$$

so that Eq. (1.148) becomes

$$p_{\alpha\beta}(0,0|0,0) = -\, 4p_1\delta_{\alpha\beta} \; . \tag{1.151b}$$

At this point we note that Eqs. (1.149) satisfy infinitesimal translation invariance explicitly, though this condition was not imposed on $p_\alpha(\ell\kappa)$ in our derivation. Only the total moment Eq. (1.130) was required to be translation invariant since we are dealing with a neutral crystal. Lattice translation invariance plus inversion symmetry then gave Eq. (1.141), which is not the same condition obtained by imposing infinitesimal translation invariance on the moments $p_\alpha(\ell\kappa)$. In fact, the definition of $p_\alpha(\ell\kappa)$ requires a volume to be associated with each atom $(\ell\kappa)$. If this volume is neutral, then the dipole moment is independent of the origin of coordinates and is translation invariant. If the volume is not neutral, then the dipole moment does depend on the origin of coordinates and is not translation invariant. The fact that Eqs. (1.49) are translation invariant without imposing this condition is a reflection of the fact that the first neighbor moment coefficients are symmetric and this together with the inversion symmetry shows that

$$p_{\alpha\beta}(0,0|\delta_i,1) = p_{\beta\alpha}(\delta_i,1|0,0) \ . \qquad (1.152)$$

Thus we see that for first neighbors, the "flip" symmetry condition Eq. (1.26) is obeyed by the moment coefficients. For second neighbors this condition need not be true. When the "flip" symmetry property is obeyed, Eq. (1.141) is then the same condition obtained by imposing infinitesimal translation invariance on the moments $p_\alpha(\ell\kappa)$.

One can explicitly verify that the total dipole moment due to Eqs. (1.149) is always zero, as we have seen it must be from Eqs. (1.133) and (1.140b). Although the total dipole moment is zero the array of dipoles can have a total quadrupole moment as shown explicitly in Appendix C.

Having determined the form of the moment coefficients, we now proceed to calculate the dipole contribution to the second order force constants. In Appendix B it is shown that for silicon we can write the interaction energy for a pair of dipoles as

$$W(\ell\kappa|\ell'\kappa') = \frac{1}{\epsilon}\sum_{\alpha,\beta}\Omega_{\alpha\beta}(\ell\kappa|\ell'\kappa')p_\alpha(\ell\kappa)p_\beta(\ell'\kappa') \tag{1.153}$$

with

$$\Omega_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \left[\frac{\delta_{\alpha\beta}}{|\vec{R}(\ell\kappa|\ell'\kappa')|^3} - \frac{3R_\alpha(\ell\kappa|\ell'\kappa')R_\beta(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|^5}\right] . \tag{1.154}$$

Here ϵ is the static dielectric constant. In writing Eq. (1.153) we have neglected short-range terms discussed in Appendix B. These terms are compensated for by the short-range contributions to the dynamical matrix.

The total dipole-dipole interaction energy is

$$\Phi^{dd} = \frac{1}{2}\sum_{\ell\kappa}\sum_{\ell'\kappa'}{}' W(\ell\kappa|\ell'\kappa') , \tag{1.155}$$

where the prime on the sum means exclude terms with $(\ell\kappa) = (\ell'\kappa')$. Using Eq. (1.17) we have

$$\Phi^{dd}_{\alpha\beta}(\ell_1\kappa_1|\ell_2\kappa_2) = \frac{1}{2} \sum_{\ell_3\kappa_3} \sum_{\ell_4\kappa_4}{}' \left[\frac{\partial^2 W(\ell_3\kappa_3|\ell_4\kappa_4)}{\partial u_\alpha(\ell_1\kappa_1)\partial u_\beta(\ell_2\kappa_2)}\right]_o , \tag{1.156}$$

where the derivatives are evaluated with all atoms in the rest positions. Using Eqs. (1.149, 1.153 and 1.154) it is a straightforward excercise to evaluate the derivatives in Eq. (1.156). We obtain the results

$$\begin{aligned}\Phi^{dd}_{\alpha\beta}(\ell_1,0|\ell_2,0) = {} & \frac{16p_1^2}{\epsilon}\Omega_{\alpha\beta}(\ell_1,0|\ell_2,0)(1-\delta_{\ell_1,\ell_2}) \\ & + \frac{1}{\epsilon} \sum_{i,j=1}^{4} \sum_{\mu,\nu} p_{\alpha\mu}(0,0|\delta_i,1)p_{\beta\nu}(0,0|\delta_j,1) \times \\ & \times \Omega_{\mu\nu}(\ell_1+\delta_i,1|\ell_2+\delta_j,1)(1-\delta_{\ell_1+\delta_i,\ell_2+\delta_j}) \\ & - \frac{1}{\epsilon} \sum_{i,j=1}^{4} \sum_{\mu,\nu} p_{\alpha\mu}(0,0|\delta_i,1)p_{\beta\nu}(0,0|\delta_j,1) \times \\ & \times \left[\Omega_{\mu\nu}(\ell_1,0|\ell_2+\delta_j,1)+\Omega_{\mu\nu}(\ell_2,0|\ell_1+\delta_i,1)\right] , \end{aligned} \tag{1.157a}$$

and

$$\Phi^{dd}_{\alpha\beta}(\ell_1,0|\ell_2,1) = \frac{16p_1^2}{\epsilon}\Omega_{\alpha\beta}(\ell_1,0|\ell_2,1)$$

$$+\frac{1}{\epsilon}\sum_{i,j=1}^{4}\sum_{\mu,\nu}p_{\alpha\mu}(0,0|\delta_i,1)p_{\beta\nu}(0,0|\delta_j,1)\Omega_{\mu\nu}(\ell_1+\delta_i,1|\ell_2-\delta_j,0)$$

$$-\frac{4p_1}{\epsilon}\sum_{i=1}^{4}\sum_{\mu}p_{\alpha\mu}(0,0|\delta_i,1)\Omega_{\mu\beta}(\ell_1+\delta_i,0|\ell_2,0)(1-\delta_{\ell_1+\delta_i,\ell_2})$$

$$-\frac{4p_1}{\epsilon}\sum_{i=1}^{4}\sum_{\mu}p_{\beta\mu}(0,0|\delta_i,1)\Omega_{\mu\alpha}(\ell_1+\delta_i,0|\ell_2,0)(1-\delta_{\ell_1+\delta_i,\ell_2})\ . \tag{1.157b}$$

The Kronecker delta symbols in Eqs. (1.157) mean omit terms when the Kronecker delta is one. Defining

$$D^{dd}_{\alpha\beta}(\kappa\kappa'|\vec{k}) = \frac{1}{M}\sum_{\ell}\Phi^{dd}_{\alpha\beta}(\ell,\kappa|0,\kappa')e^{-i\vec{k}\cdot\vec{R}(\ell)} \tag{1.158}$$

we find

$$D^{dd}_{\alpha\beta}(0,0|\vec{k}) = \frac{16p_1^2}{\epsilon M}\sum_{\ell}\Omega_{\alpha\beta}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)}(1-\delta_{\ell,0})$$

$$+\frac{1}{\epsilon M}\sum_{\mu,\nu}\sum_{\ell}F_{\alpha\mu}(\vec{k})F^{*}_{\beta\nu}(\vec{k})\Omega_{\mu\nu}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)}(1-\delta_{\ell,0})$$

$$-\frac{4p_1}{\epsilon M}\sum_{\mu}\sum_{\ell}F^{*}_{\beta\mu}(\vec{k})\Omega_{\mu\alpha}(\ell,0|0,1)e^{-i\vec{k}\cdot\vec{R}(\ell)}$$

$$-\frac{4p_1}{\epsilon M}\sum_{\mu}\sum_{\ell}F_{\alpha\mu}(\vec{k})\Omega_{\mu\beta}(\ell,0|0,1)e^{+i\vec{k}\cdot\vec{R}(\ell)}\ , \tag{1.159a}$$

and

$$D^{dd}_{\alpha\beta}(0,1|\vec{k}) = \frac{16p_1^2}{\epsilon M}\sum_{\ell}\Omega_{\alpha\beta}(\ell,0|0,1)e^{-i\vec{k}\cdot\vec{R}(\ell)}$$

$$+\frac{1}{\epsilon M}\sum_{\mu,\nu}\sum_{\ell}F_{\alpha\mu}(\vec{k})F_{\beta\nu}(\vec{k})\Omega_{\mu\nu}(\ell,1|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)}$$

$$-\frac{4p_1}{\epsilon M}\sum_{\mu}\sum_{\ell}F_{\alpha\mu}(\vec{k})\Omega_{\mu\beta}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)}(1-\delta_{\ell,0})$$

$$-\frac{4p_1}{\epsilon M}\sum_{\mu}\sum_{\ell}F_{\beta\mu}(\vec{k})\Omega_{\mu\alpha}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)}(1-\delta_{\ell,0}) \; , \tag{1.159b}$$

where we have defined

$$F_{\alpha\beta}(\vec{k}) = \sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1)e^{i\vec{k}\cdot\vec{\delta}_i} \; . \tag{1.160}$$

Decomposing $F_{\alpha\beta}(\vec{k})$ as

$$F_{\alpha\beta}(\vec{k}) = [p_1 S(\vec{k})\delta_{\alpha\beta} + p_2 S_{\alpha\beta}(\vec{k})] \tag{1.161}$$

we have

$$S(\vec{k}) = (1+e^{i\vec{k}\cdot\vec{\delta}_2}+e^{i\vec{k}\cdot\delta_3}+e^{i\vec{k}\cdot\vec{\delta}_4}) \tag{1.162}$$

and

$$\bar{\bar{S}}(\vec{k}) = \begin{pmatrix} 0 & S_{12} & S_{13} \\ S_{12} & 0 & S_{23} \\ S_{13} & S_{23} & 0 \end{pmatrix} , \tag{1.163}$$

with

$$S_{12} = (1+e^{i\vec{k}\cdot\vec{\tau}_2}-e^{i\vec{k}\cdot\vec{\tau}_3}-e^{i\vec{k}\cdot\vec{\tau}_4}) \qquad (1.164a)$$

$$S_{13} = (1-e^{i\vec{k}\cdot\vec{\tau}_2}-e^{i\vec{k}\cdot\vec{\tau}_3}+e^{i\vec{k}\cdot\vec{\tau}_4}) \qquad (1.164b)$$

$$S_{23} = (1-e^{i\vec{k}\cdot\vec{\tau}_2}+e^{i\vec{k}\cdot\vec{\tau}_3}-e^{i\vec{k}\cdot\vec{\tau}_4}) \ . \qquad (1.164c)$$

The dipole contribution to the dynamical matrix can be written in a more compact form as follows

$$D^{dd}_{\alpha\beta}(0,0|\vec{k}) = \frac{4\pi p_1^2}{\epsilon M\Omega_o} T^{11}_{\alpha\beta}(\vec{k}) + \frac{4\pi p_1 p_2}{\epsilon M\Omega_o} T^{12}_{\alpha\beta}(\vec{k}) + \frac{4\pi p_2^2}{\epsilon M\Omega_o} T^{22}_{\alpha\beta}(\vec{k}) \qquad (1.165a)$$

$$D^{dd}_{\alpha\beta}(0,1|\vec{k}) = \frac{4\pi p_1^2}{\epsilon M\Omega_o} V^{11}_{\alpha\beta}(\vec{k}) + \frac{4\pi p_1 p_2}{\epsilon M\Omega_o} V^{12}_{\alpha\beta}(\vec{k}) + \frac{4\pi p_2^2}{\epsilon M\Omega_o} V^{22}_{\alpha\beta}(\vec{k}) \ . \qquad (1.165b)$$

The dimensionless matrices T and V are defined as

$$T^{11}_{\alpha\beta}(\vec{k}) = \frac{\Omega}{4\pi}\left\{\begin{array}{l} [16+S^*(\vec{k})S(\vec{k})]\sum_{\ell}{}' \Omega_{\alpha\beta}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \\ - 4S^*(\vec{k})\sum_{\ell}\Omega_{\alpha\beta}(\ell,0|0,1)e^{-i\vec{k}\cdot\vec{R}(\ell)} \\ - 4S(\vec{k})\sum_{\ell}\Omega_{\alpha\beta}(\ell,0|0,1)e^{+i\vec{k}\cdot\vec{R}(\ell)} \end{array}\right\}$$

(1.166a)

$$T^{12}_{\alpha\beta}(\vec{k}) = \frac{\Omega_o}{4\pi}\left[\begin{aligned} & S(\vec{k})\sum_{\mu} S^{*}_{\beta\mu}(\vec{k})\sum_{\ell}{}' \,\Omega_{\mu\alpha}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \\ & + S^{*}(\vec{k})\sum_{\mu} S_{\alpha\mu}(\vec{k})\sum_{\ell}{}' \,\Omega_{\mu\beta}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \\ & - 4\sum_{\mu} S^{*}_{\beta\mu}(\vec{k})\sum_{\ell}\Omega_{\mu\alpha}(\ell,0|0,1)e^{-i\vec{k}\cdot\vec{R}(\ell)} \\ & - 4\sum_{\mu} S_{\alpha\mu}(\vec{k})\sum_{\ell}\Omega_{\mu\beta}(\ell,0|0,1)e^{+i\vec{k}\cdot\vec{R}(\ell)} \end{aligned}\right] \tag{1.166b}$$

$$T^{22}_{\alpha\beta}(\vec{k}) = \frac{\Omega_o}{4\pi}\sum_{\mu,\nu} S_{\alpha\mu}(\vec{k})S^{*}_{\beta\nu}(\vec{k})\sum_{\ell}{}' \,\Omega_{\mu\nu}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \tag{1.166c}$$

$$V^{11}_{\alpha\beta}(\vec{k}) = \frac{\Omega_o}{4\pi}\left[\begin{aligned} & 16\sum_{\ell}\Omega_{\alpha\beta}(\ell,0|0,1)e^{-ik\cdot\vec{R}(\ell)} \\ & + S^{2}(\vec{k})\sum_{\ell}\Omega_{\alpha\beta}(\ell,1|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \\ & - 8S(\vec{k})\sum_{\ell}{}' \,\Omega_{\alpha\beta}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \end{aligned}\right] \tag{1.167a}$$

$$V^{12}_{\alpha\beta}(\vec{k}) = \frac{\Omega_o}{4\pi}\left[\begin{aligned} & S(\vec{k})\sum_{\mu} S_{\beta\mu}(\vec{k})\sum_{\ell}\Omega_{\mu\alpha}(\ell,1|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \\ & + S(\vec{k})\sum_{\mu} S_{\alpha\mu}(\vec{k})\sum_{\ell}\Omega_{\mu\beta}(\ell,1|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \\ & - 4\sum_{\mu} S_{\alpha\mu}(\vec{k})\sum_{\ell}{}' \,\Omega_{\mu\beta}(\ell,0|0,0)e^{-\quad\cdot\vec{R}(\ell)} \\ & - 4\sum_{\mu} S_{\beta\mu}(\vec{k})\sum_{\ell}{}' \,\Omega_{\mu\alpha}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \end{aligned}\right] \tag{1.167b}$$

$$V^{22}_{\alpha\beta}(\vec{k}) = \frac{\Omega_0}{4\pi} \sum_{\mu,\nu} S_{\alpha\mu}(\vec{k}) S_{\beta\nu}(\vec{k}) \sum_{\ell} \Omega_{\mu\nu}(\ell,1|0\ 0) e^{-i\vec{k}\cdot\vec{R}(\ell)} \quad . \tag{1.167c}$$

In Eqs. (1.166) and (1.167) there are three long-range sums to perform, two of which are related, namely

$$Q^{(1)}_{\alpha\beta}(\vec{k}) = \frac{\Omega_0}{4\pi} \sum_{\ell}{}' \ \Omega_{\alpha\beta}(\ell,0|0,0) e^{-i\vec{k}\cdot\vec{R}(\ell)} \tag{1.168a}$$

$$Q^{(2)}_{\alpha\hat{\beta}}(\vec{k}) = \frac{\Omega_0}{4\pi} \sum_{\ell} \ \Omega_{\alpha\hat{\beta}}(\ell,0|0,1) e^{-i\vec{k}\cdot\vec{R}(\ell)} \tag{1.168b}$$

$$Q^{(2)*}_{\alpha\hat{\beta}}(\vec{k}) = \frac{\Omega_0}{4\pi} \sum_{\ell} \ \Omega_{\alpha\hat{\beta}}(\ell,1|0,0) e^{-i\vec{k}\cdot\vec{R}(\ell)} \quad . \tag{1.168c}$$

These sums are slowly convergent for numerical work. In Appendix D we discuss the Ewald method of transforming these sums to rapidly convergent form. The Ewald method also has the advantage of allowing explicit separation of the nonanalytic behaviour of Eqs. (1.168) which enables one to show that the dipole contribution to the dynamical matrix is analytic at $\vec{k} = 0$, even though the separate contributions to it are not.

PHONON FREQUENCIES ALONG SYMMETRY DIRECTIONS

In this section we present expressions for the dynamical matrix and for phonon frequencies along the [100], [110] and [111] directions. We also give expressions for the elastic constants using the model developed in the previous sections.

[100] Direction

Along the [100] direction the wavevector $\vec{k}$ is

$$\vec{k} = k\hat{e}_1 \ . \tag{1.169}$$

Direct computation using the model developed in previous sections allows one to write the dynamical matrix along [100] as

$$[D_{\alpha\beta}(\kappa\kappa'|k)] = \begin{pmatrix} A_1 & 0 & 0 & A_3 & 0 & 0 \\ 0 & A_2 & 0 & 0 & A_4 & A_5 \\ 0 & 0 & A_2 & 0 & A_5 & A_4 \\ A_3^* & 0 & 0 & A_1 & 0 & 0 \\ 0 & A_4^* & A_5^* & 0 & A_2 & 0 \\ 0 & A_5^* & A_4^* & 0 & 0 & A_2 \end{pmatrix} \tag{1.170}$$

where A_1 and A_2 are real and we have defined

$$A_1 = A + D_{11}^{dd}(0,0|k) \tag{1.171a}$$

$$A_2 = B + D_{22}^{dd}(0,0|k) \tag{1.171b}$$

$$A_3 = C + D^{dd}_{11}(0,1|k) \tag{1.171c}$$

$$A_4 = D + D^{dd}_{22}(0,1|k) \tag{1.171d}$$

$$A_5 = E + D^{dd}_{23}(0,1|k) \tag{1.171e}$$

and

$$A = \frac{1}{M}\left|4\alpha+16\mu\sin^2\frac{ka}{4}+8\mu'+4\lambda'+4\lambda''\sin^2\frac{ka}{2}+12\sigma-\frac{4\sigma}{3}\cos\frac{ka}{2}\right| \tag{1.172a}$$

$$B = \frac{1}{M}\left[\begin{array}{l}4\alpha+8(\mu+\lambda)\sin^2\frac{ka}{4}+(8\mu'+4\lambda')+4\mu''\sin^2\frac{ka}{2}\\ +\frac{26\sigma}{3}+2\sigma\cos\frac{ka}{2}\end{array}\right] \tag{1.172b}$$

$$C = -\frac{1}{M}\left[(2\alpha+4\mu'+\frac{16\sigma}{3})(1+e^{-ika/2})+2\lambda'(e^{ika/2}+e^{-ika})\right] \tag{1.172c}$$

$$D = -\frac{1}{M}\left[\begin{array}{l}(2\alpha+2\lambda'+\frac{16\sigma}{3})(1+e^{-ika/2})+2\mu'(1+e^{ika/2}+\\ +e^{-ika/2}+e^{-ika})\end{array}\right] \tag{1.172d}$$

$$E = \frac{1}{M}\left[(-2\beta+4\delta'+\frac{8\sigma}{3})(1-e^{-ika/2})+2\nu'(e^{ika/2}-e^{-ika})\right] . \tag{1.172e}$$

We now proceed to find the eigenvalues of Eq. (1.170) using the eigenvectors of Lax.[45] It is important to note that his eigenvectors correspond to the second form of the dynamical matrix which uses displacements of the form

$$u_\alpha(\ell\kappa) = \frac{V_\alpha(\kappa)}{\sqrt{M}}\, e^{i\vec{k}\cdot\vec{R}(\ell\kappa)-i\omega t} , \tag{1.173}$$

and differs by a phase factor from Eq. (1.19). Thus we have

$$W_\alpha(\kappa) = V_\alpha(\kappa)e^{i\vec{k}\cdot\vec{R}(\kappa)} , \tag{1.174}$$

where $W_\alpha(\kappa)$ is defined by Eq. (1.19). The $V_\alpha(\kappa)$ are given by Lax for the [100], [110] and [111] directions.

Consider first the longitudinal modes. Noting that along [100]

$$e^{i\vec{k}\cdot\vec{R}(1)} = e^{ika/4} \tag{1.175}$$

we have for the longitudinal acoustic (LA) Δ_1 mode

$$W_\alpha(0) = b\delta_{\alpha 1} \tag{1.176a}$$

$$W_\alpha(1) = e^{ika/4}b\delta_{\alpha 1} . \tag{1.176b}$$

Substituting Eqs. (1.176) into Eq. (1.20) and using Eq. (1.170) we obtain

$$\omega^2 b = (A_1 + A_3 e^{ika/4})b \tag{1.177a}$$

$$\omega^2 b = (A_1 + A_3^* e^{-ika/4})b . \tag{1.177b}$$

For this to be a solution we must have that

$$A_3 e^{ika/4} = \text{purely real}. \tag{1.178}$$

This is in fact the case so that

$$\omega^2_{LA[100]} = [A_1 + \mathrm{Re}(e^{ika/4}A_3)] \ . \tag{1.179}$$

After some algebra we obtain

$$\begin{aligned}\omega^2_{LA[100]} &= \frac{(8\alpha+16\mu'+64\sigma/3)}{M}\sin^2\frac{ka}{8} \\ &+ \frac{(16\mu+8\sigma/3)}{M}\sin^2\frac{ka}{4} + \frac{8\lambda'}{M}\sin^2\frac{3ka}{8} \\ &+ \frac{4\lambda''}{M}\sin^2\frac{ka}{2} + \frac{4\pi p_1^2}{\epsilon M\Omega_o}[T^{11}_{11}(k)+\mathrm{Re}(e^{ika/4}V^{11}_{11}(k))] \ ,\end{aligned} \tag{1.180}$$

and we have used the facts that

$$T^{12}_{11}(k) = T^{22}_{11}(k) = V^{12}_{11}(k) = V^{22}_{11}(k) = 0 \tag{1.181}$$

along [100] and

$$T^{11}_{11}(k) = \text{purely real.} \tag{1.182}$$

We can obtain an expression for the elastic constant C_{11} from Eq. (1.180) by using the fact that for $ka \ll 1$

$$\omega^2_{LA[100]} = \left(\frac{C_{11}}{\rho}k^2\right) + \left(\begin{matrix}\text{higher order}\\ \text{in ka}\end{matrix}\right) \tag{1.183}$$

so that

$$aC_{11} = (\alpha + 4\sigma + 8\mu + 2\mu' + 9\lambda' + 8\lambda'') \ . \tag{1.184}$$

Note that the dipole terms are absent from Eq. (1.184). This is an important point and is a consequence of the non-local nature of the dipoles. In order to see this, we only need show that along [100]

$$\frac{\partial}{\partial k}\left[T_{11}^{11}(k) + \mathrm{Re}(e^{ika/4}V_{11}^{11}(k))\right]\bigg|_{k=0} = 0 \qquad (1.185a)$$

and

$$\frac{\partial^2}{\partial k^2}\left[T_{11}^{11}(k) + \mathrm{Re}(e^{ika/4}V_{11}^{11}(k))\right]\bigg|_{k=0} = 0\ . \qquad (1.185b)$$

This is in fact the case as shown in Appendix E.

Consider next the longitudinal optic (LO) Δ_2' mode. for this mode

$$W_\alpha(0) = b\delta_{\alpha 1} \qquad (1.186a)$$

$$W_\alpha(1) = -\ e^{ika/4}b\delta_{\alpha 1}\ . \qquad (1.186b)$$

Substituting Eqs. (1.186) into Eq. (1.20) and using Eq. (1.170) we obtain

$$\omega^2 b = (A_1 - A_3 e^{ika/4})b \qquad (1.187a)$$

$$\omega^2 b = (A_1 - A_3^* e^{-ika/4})b \qquad (1.187b)$$

using Eq. (1.178) we have

$$\omega^2_{LO[100]} = [A_1 - \mathrm{Re}(e^{ika/4}A_3)] \ . \qquad (1.188)$$

After some algebra we obtain

$$\omega^2_{LO[100]} = \frac{(4\alpha+8\mu'+32\sigma/3)}{M}(1+\cos\frac{ka}{4}) + \frac{16\mu}{M}\sin^2\frac{ka}{4}$$

$$+ \frac{4\lambda'}{M}(1+\cos\frac{3ka}{4}) + \frac{4\lambda''}{M}\sin^2\frac{ka}{2} + \frac{4\sigma}{3M}(1-\cos\frac{ka}{2})$$

$$+ \frac{4\pi p_1^2}{\epsilon M\Omega_o}[T^{11}_{11}(k) - \mathrm{Re}(e^{ika/4}V^{11}_{11}(k))] \ . \qquad (1.189)$$

At $\vec{k} = 0$ $\omega_{LO[100]}$ becomes the Raman frequency, denoted ω_{RA} , so that

$$\omega^2_{RA} = (8\alpha + 64\sigma/3 + 16\mu' + 8\lambda')/M \ . \qquad (1.190)$$

In obtaining Eq. (1.190) we have made use of the fact that

$$T^{11}_{11}(k=0) = \mathrm{Re}\ V^{11}_{11}(k=0) = 0 \ . \qquad (1.191)$$

Note that the dipoles do not contribute to the Raman frequency, which is again a consequence of the nonlocal nature of the dipoles. This is in marked contrast to the local quadrupoles used by Lax[46] which do contribute to both C_{11} and ω_{RA} .

Furthermore, at the X point of the Brillouin zone boundary $k = \frac{2\pi}{a}$, so that we find from Eqs. (1.180) and (1.189)

$$\omega^2_{LOX} = \omega^2_{LAX} = \frac{1}{M}(4\alpha+40\sigma/3+16\mu+8\mu'+4\lambda') + \frac{4\pi p_1^2}{\varepsilon M\Omega_0} T^{11}_{11}(X) \tag{1.192a}$$

where

$$T^{11}_{11}(X) = 5.51804915 \ . \tag{1.192b}$$

In obtaining Eq. (1.192a) we have used the fact that $V^{11}_{11}(X) = 0$.

Now we proceed to the transverse modes. These modes are labeled Δ_5 and are doubly degenerate. One eigenvector is

$$W_\alpha(0) = a(\delta_{\alpha 2} - \delta_{\alpha 3}) \tag{1.193a}$$

$$W_\alpha(1) = e^{ika/4} b(\delta_{\alpha 2} - \delta_{\alpha 3}) \ . \tag{1.193b}$$

Substituting Eqs. (1.193) into Eq. (1.20) and using Eq. (1.170) we obtain the secular equation for the transverse modes

$$\omega^2_{T[100]\pm} = A_2 \pm [(A_4-A_5)e^{ika/4}(A_4^*-A_5^*)e^{-ka/4}]^{\frac{1}{2}} \ . \tag{1.194}$$

We can rewrite Eq. (1.194) as

$$\omega^2_{T[100]\pm} = B + D^{dd}_{22}(0,0|k) \pm \left\{ \begin{array}{l} [\mathrm{Re}(De^{ika/4})+\mathrm{Re}(e^{ika/4}D^{dd}_{22}(0,1|k))]^2 \\ +[\mathrm{Im}(Ee^{ika/4})+\mathrm{Im}(e^{ika/4}D^{dd}_{23}(0,1|k))]^2 \end{array} \right\}^{\frac{1}{2}} \tag{1.195}$$

where we note that

$$De^{ika/4} = -\frac{1}{M}\left[(4\alpha+4\mu'+4\lambda'+32\sigma/3)\cos\frac{ka}{4} + 4\mu'\cos\frac{3ka}{4}\right] \tag{1.196a}$$

$$Ee^{ika/4} = \frac{i}{M}\left[(16\sigma/3+8\delta'-4\beta)\sin\frac{ka}{4} + 4\nu'\sin\frac{3ka}{4}\right] \tag{1.196b}$$

and

$$D^{dd}_{22}(0,1|k)e^{ika/4} = \mathrm{Re}(e^{ika/4}D^{dd}_{22}(0,1|k)) \tag{1.197a}$$

$$D^{dd}_{23}(0,1|k)e^{ika/4} = i\,\mathrm{Im}(e^{ika/4}D^{dd}_{23}(0,1|k))\ . \tag{1.197b}$$

To obtain an expression for the elastic constant C_{44} we use the fact that for $ka \ll 1$

$$\omega^2_{TA[100]} = \left(\frac{C_{44}}{\rho}k^2\right) + \left(\begin{array}{c}\text{higher order} \\ \text{in } ka\end{array}\right) \tag{1.198}$$

so that

$$aC_{44} = \alpha + \frac{2c}{3} + 4\mu + 4\lambda + \lambda' + 10\mu' + 8\mu''$$

$$- \frac{(4\sigma/3-\beta+2\delta'+3\nu')^2}{(\alpha+8\sigma/3+2\mu'+\lambda')} . \qquad (1.199)$$

In obtaining Eq. (1.199) we have used the fact that the lower sign in Eq. (1.195) corresponds to the acoustic branch. Note again that the dipole terms do not contribute to C_{44} .

At the X point of the Brillouin zone boundary we find from Eq. (1.195) that

$$\omega_{TAX}^2 = \frac{1}{M}(4\alpha-4\beta+8\mu+8\lambda+8\mu'+4\lambda'-4\nu'+8\delta'+12\sigma)$$

$$+ \frac{4\pi(p_1-p_2)^2}{\epsilon M\Omega_o}(T_{22}^{11}(X)+V_{23}^{11}(X)) \qquad (1.200)$$

and

$$\omega_{TOX}^2 = \frac{1}{M}(4\alpha+4\beta+8\mu+8\lambda+8\mu'+4\lambda'+4\nu'-8\delta'+4\sigma/3)$$

$$+ \frac{4\pi(p_1+p_2)^2}{\epsilon M\Omega_o}(T_{22}^{11}(X)-V_{23}^{11}(X)) \qquad (1.201)$$

where

$$T_{22}^{11}(X) = -2.75902458 \qquad (1.202a)$$

$$V_{23}^{11}(X) = -13.5224054 . \qquad (1.202b)$$

In obtaining Eqs. (1.200) and (1.201) we have used the relations

$$V_{23}^{11}(X) = V_{23}^{22}(X) \tag{1.203a}$$

$$T_{22}^{11}(X) = T_{22}^{22}(X) \tag{1.203b}$$

$$T_{22}^{12}(X) = -2V_{23}^{11}(X) \tag{1.203c}$$

$$V_{23}^{12}(X) = -2T_{22}^{11}(X) \ . \tag{1.203d}$$

The dipoles strongly affect the zone boundary modes. They push the transverse optic (TO) mode up and lower the frequency of the transverse acoustic (TA) mode.

[110] Direction

Along the [110] direction the wavevector $\vec{k}$ is

$$\vec{k} = \frac{k}{\sqrt{2}}(\hat{e}_1 + \hat{e}_2) \tag{1.204}$$

where $k = |\vec{k}|$. Direct computation using the model developed in previous sections allows one to write the dynamical matrix along [110] as

$$[D_{\alpha\beta}(\kappa\kappa'|k)] = \begin{pmatrix} B_1 & B_2 & B_3 & B_5 & B_6 & B_7 \\ B_2 & B_1 & B_3 & B_6 & B_5 & B_7 \\ B_3^* & B_3^* & B_4 & B_7 & B_7 & B_8 \\ B_5^* & B_6^* & B_7^* & B_1 & B_2 & B_3^* \\ B_6^* & B_5^* & B_7^* & B_2 & B_1 & B_3^* \\ B_7^* & B_7^* & B_8^* & B_3 & B_3 & B_4 \end{pmatrix} \tag{1.205}$$

where B_1, B_2 and B_4 are real, B_3 is purely imaginary and we have defined

$$B_1 = A + D_{11}^{dd}(0,0|k) \tag{1.206a}$$

$$B_2 = B + D_{12}^{dd}(0,0|k) \tag{1.206b}$$

$$B_3 = C + D_{13}^{dd}(0,0|k) \tag{1.206c}$$

$$B_4 = D + D_{33}^{dd}(0,0|k) \tag{1.206d}$$

$$B_5 = E + D_{11}^{dd}(0,1|k) \tag{1.206e}$$

$$B_6 = F + D_{12}^{dd}(0,1|k) \tag{1.206f}$$

$$B_7 = G + D_{13}^{dd}(0,1|k) \tag{1.206g}$$

$$B_8 = H + D_{33}^{dd}(0,1|k) \tag{1.206h}$$

and

$$A = \frac{1}{M}\left[\begin{aligned} &4\alpha+8(\mu+\lambda)\sin^2\frac{ka}{4\sqrt{2}} + 4\mu\sin^2\frac{ka}{2\sqrt{2}} + 8\mu' + 4\lambda' \\ &+ 4(\mu''+\lambda'')\sin^2\frac{ka}{2\sqrt{2}} + 9\sigma + 2\sigma\cos\frac{ka}{2\sqrt{2}} \\ &- \sigma/3\cos\frac{ka}{\sqrt{2}} \end{aligned}\right] \tag{1.207a}$$

$$B = \frac{1}{M}(4\nu + 2\sigma/3)\sin^2\frac{ka}{2\sqrt{2}} \tag{1.207b}$$

$$C = \frac{i}{M}\left(\frac{4\sigma}{3}\sin\frac{ka}{2\sqrt{2}} - \frac{2\sigma}{3}\sin\frac{ka}{\sqrt{2}}\right) \tag{1.207c}$$

$$D = \frac{1}{M}\left[\begin{array}{l} 4\alpha + 16\mu \sin^2 \frac{ka}{4\sqrt{2}} + 4\lambda \sin^2 \frac{ka}{2\sqrt{2}} \\ + 8\mu' + 4\lambda' + 8\mu'' \sin^2 \frac{ka}{2\sqrt{2}} + \frac{32\sigma}{3} \\ + \frac{4\sigma}{3} \cos \frac{ka}{\sqrt{2}} - \frac{4\sigma}{3} \cos \frac{ka}{2\sqrt{2}} \end{array}\right] \tag{1.207d}$$

$$E = -\frac{1}{M}\left[\begin{array}{l} (\alpha+8\sigma/3)(1+2e^{-ika/2\sqrt{2}}+e^{-ika/\sqrt{2}}) \\ + \mu'(2+2e^{-ika/2\sqrt{2}}+2e^{-ika/\sqrt{2}}+e^{ika/2\sqrt{2}}+e^{-3ika/2\sqrt{2}}) \\ + \lambda'(1+e^{-ika/\sqrt{2}}+e^{ika/2\sqrt{2}}+e^{-3ika/2\sqrt{2}}) \end{array}\right] \tag{1.207e}$$

$$F = \frac{1}{M}\left[\begin{array}{l} (-\beta+4\sigma/3)(1+e^{-ika/\sqrt{2}}-2e^{-ika/2\sqrt{2}}) \\ + 2\delta'(1+e^{-ika/\sqrt{2}}-e^{ika/2\sqrt{2}}-e^{-3ika/2\sqrt{2}}) \\ - \nu'(1-2e^{-ika/2\sqrt{2}}+e^{-ika/\sqrt{2}}) \end{array}\right] \tag{1.207f}$$

$$G = \frac{1}{M}\left[\begin{array}{l} (-\beta+4\sigma/3)(1-e^{-ika/\sqrt{2}})+\delta'(e^{ika/2\sqrt{2}}-e^{-3ika/2\sqrt{2}}) \\ + \nu'(1+e^{ika/2\sqrt{2}}-e^{-ika/\sqrt{2}}-e^{-3ika/2\sqrt{2}}) \end{array}\right] \tag{1.207g}$$

$$H = -\frac{1}{M}\left[\begin{array}{l} (\alpha+\lambda'+8\sigma/3)(1-e^{-ika/\sqrt{2}}+2e^{-ika/2\sqrt{2}}) \\ + 2\mu'(1+e^{-ika/\sqrt{2}}+e^{ika/2\sqrt{2}}+e^{-3ika/2\sqrt{2}}) \end{array}\right] . \tag{1.207h}$$

Now consider the modes whose eigenvectors are determined by symmetry alone. Noting that along [110]

$$e^{i\vec{k}\cdot\vec{R}(1)} = e^{ika/2\sqrt{2}} \qquad (1.208)$$

we have for the Σ_4 mode which is $TA_{\perp z}$

$$W_\alpha(0) = b(\delta_{\alpha 1}-\delta_{\alpha 2}) \qquad (1.209a)$$

$$W_\alpha(1) = e^{ika/2\sqrt{2}}b(\delta_{\alpha 1}-\delta_{\alpha 2}) \ . \qquad (1.209b)$$

Here $TA_{\perp z}$ denotes that the Σ_4 mode is transverse acoustic and polarized perpendicular to the z axis as well as to the direction of propagation. Substituting Eqs. (1.209) into Eq. (1.20) and using Eq. (1.205) we obtain

$$\omega^2 b = [B_1-B_2+e^{ika/2\sqrt{2}}(B_5-B_6)]b \qquad (1.210a)$$

$$\omega^2 b = [B_1-B_2+e^{-ika/2\sqrt{2}}(B_5^*-B_6^*)]b \ . \qquad (1.210b)$$

For this to be a solution we must have that

$$e^{ika/2\sqrt{2}}(B_5-B_6) = \text{purely real.} \qquad (1.211)$$

This is in fact the case so that

$$\omega^2_{\Sigma_4} = B_1-B_2 + \mathrm{Re}[e^{ika/2\sqrt{2}}(B_5-B_6)] \ . \qquad (1.212)$$

After some algebra we obtain

$$\omega^2_{\Sigma_4} = \frac{1}{M}(4\alpha-4\beta+8\mu+8\lambda+8\mu'-4\nu'+4\lambda'+8\delta'+12\sigma)\sin^2\frac{ka}{4\sqrt{2}}$$

$$+\frac{1}{M}(4\mu-4\nu+4\mu'+4\lambda'-8\delta'+4\mu''+4\lambda'')\sin^2\frac{ka}{2\sqrt{2}}$$

$$+D^{dd}_{11}(0,0|k)-D^{dd}_{12}(0,0|k)+\mathrm{Re}(e^{ika/2\sqrt{2}}D^{dd}_{11}(0,1|k))$$

$$-\mathrm{Re}(e^{ika/2\sqrt{2}}D^{dd}_{12}(0,1|k)) \ . \qquad (1.213)$$

Note that $D^{dd}_{11}(0,0|k)$ and $D^{dd}_{12}(0,0|k)$ are purely real along [110]. We can obtain an expression for the elastic constant C_{12} by using the fact that the Σ_4 mode is the "slow" TA mode in the elastic region[47] so that for $ka \ll 1$

$$\omega^2_{\Sigma_4} = \frac{(C_{11}-C_{12})}{2\rho}k^2 + \begin{pmatrix}\text{higher order}\\ \text{in ka}\end{pmatrix} \ . \qquad (1.214)$$

Using Eq. (1.213) and the expression for C_{11}, Eq. (1.184), we find that

$$aC_{12} = (2\beta-\alpha-2\sigma+8\nu-4\mu-4\lambda-10\mu'+2\nu'-\lambda'+12\delta'-8\mu'') \ . \qquad (1.215)$$

From the expression for the bulk modulus B

$$B = \frac{1}{3}(C_{11}+2C_{12}) \qquad (1.216)$$

we obtain using Eqs. (1.184) and (1.215) that

$$B = \frac{1}{3a}\left[4\beta-\alpha+16\nu-8\lambda-18\mu'+4\nu'+7\lambda'+24\delta'+8\lambda''-16\mu''\right] . \tag{1.217}$$

Note that the dipole terms do not contribute to C_{12} and that the bulk modulus is independent of the angle bending interaction. We can see in a simple way why the dipoles do not affect C_{12} . Since the dipoles do not affect C_{11} , if they do not affect the bulk modulus, then by Eq. (1.216) we see that they will not affect C_{12} . The reason that the dipoles do not contribute to the bulk modulus follows from the fact that a homogeneous isotropic deformation induces no dipole moments and thus no dipole-dipole interaction energy for this type of deformation.

Next consider the Σ_2 mode which is $TO_{\perp z}$. For this mode

$$W_\alpha(0) = b(\delta_{\alpha 1}-\delta_{\alpha 2}) \tag{1.218a}$$

$$W_\alpha(1) = e^{ika/2\sqrt{2}}b(-\delta_{\alpha 1}+\delta_{\alpha 2}) . \tag{1.218b}$$

Substituting Eqs. (1.218) into Eq. (1.20) and using Eq. (1.205) we obtain

$$\omega^2 b = [B_1-B_2+e^{ika/2\sqrt{2}}(B_6-B_5)]b \tag{1.219a}$$

$$\omega^2 b = [B_1-B_2 + e^{-ika/2\sqrt{2}}(B_6^*-B_5^*)]b . \tag{1.219b}$$

Using Eq. (1.211) we have

$$\omega^2_{\Sigma_2} = B_1 - B_2 + \mathrm{Re}[e^{ika/2\sqrt{2}}(B_6 - B_5)] \ . \qquad (1.220)$$

After some algebra we obtain

$$\begin{aligned}\omega^2_{\Sigma_2} = \frac{1}{M}\Bigg[& (6\alpha+10\mu'+2\nu'+4\lambda'+34\sigma/3) \\ & + (2\alpha+4\mu'+4\delta'+2\lambda'+10\sigma)\cos\frac{ka}{2\sqrt{2}} \\ & + (2\mu'+2\lambda'-2\nu'-4\delta')\cos\frac{ka}{\sqrt{2}} \\ & + (4\beta+8\mu+8\lambda)\sin^2\frac{ka}{4\sqrt{2}} + (4\mu-4\nu+4\mu''+4\lambda'')\sin^2\frac{ka}{2\sqrt{2}} \\ & + D^{dd}_{11}(0,0|k) - D^{dd}_{12}(0,0|k) + \mathrm{Re}(e^{ika/2\sqrt{2}}D^{dd}_{12}(0,1|k)) \\ & - \mathrm{Re}(e^{ika/2\sqrt{2}}D^{dd}_{11}(0,1|k)) \Bigg] .\end{aligned} \qquad (1.221)$$

Now we examine the modes that are two dimensional representations. The modes are mixed modes and are not purely longitudinal or purely transverse. First consider the Σ_1 modes which are a mixture of LA + TO_z , where TO_z denotes transverse optic polarized in the z direction. For these modes

$$W_\alpha(0) = b(\delta_{\alpha 1}+\delta_{\alpha 2}) + c\delta_{\alpha 3} \qquad (1.222a)$$

$$W_\alpha(1) = e^{ika/2\sqrt{2}}[(\delta_{\alpha 1}+\delta_{\alpha 2}) - c\delta_{\alpha 3}] \ . \qquad (1.222b)$$

Substituting Eqs. (1.222) into Eq. (1.20) and using Eq.

(1.205) we obtain the secular equation

$$\omega^2_{\Sigma_3^\pm} = \frac{1}{2}\left\{B_1+B_2+B_4+\mathrm{Re}\left[e^{ika/2\sqrt{2}}(B_5+B_6+B_8)\right]\right\}$$
$$\frac{1}{2}\left[\left\{B_1+B_2-B_4+\mathrm{Re}\left[e^{ika/2\sqrt{2}}(B_5+B_6+B_8)\right]\right\}^2 + 8\left[\mathrm{Im}\left(B_3-e^{ika/2\sqrt{2}}B_7\right)\right]^2\right]^{\frac{1}{2}} \quad . \tag{1.223}$$

In obtaining Eq. (1.223) we have used the facts that $B_1, B_2, B_4, B_5e^{ika/2\sqrt{2}}, B_6e^{ika/2\sqrt{2}}$, and $B_8e^{ika/2\sqrt{2}}$ are purely real and that B_3 and $B_7e^{ika/2\sqrt{2}}$ are purely imaginary. The upper sign in Eq. (1.223) is the optical branch and the lower sign the acoustic branch.

Similarly, the Σ_3 modes are a mixture of LO + TA$_z$. For these modes

$$W_\alpha(0) = b(\delta_{\alpha1}+\delta_{\alpha2}) + c\delta_{\alpha3} \tag{1.224a}$$

$$W_\alpha(1) = e^{ika/2\sqrt{2}}[-b(\delta_{\alpha1}+\delta_{\alpha2})+c\delta_{\alpha3}] \quad . \tag{1.224b}$$

In a similar fashion to Eq. (1.223) we obtain the secular equation

$$\omega^2_{\Sigma_2^\pm} = \frac{1}{2}\left\{B_1+B_2+B_4-\mathrm{Re}\left[e^{ika/2\sqrt{2}}(B_5+B_6-B_8)\right]\right\}$$
$$\pm\frac{1}{2}\left[\left\{B_1+B_2-B_4-\mathrm{Re}\left[e^{ika/2\sqrt{2}}(B_5+B_6+B_8)\right]\right\}^2 + 8\left[\mathrm{Im}\left(B_3+B_7e^{ika/2\sqrt{2}}\right)\right]^2\right]^{\frac{1}{2}} \quad . \tag{1.225}$$

The upper sign in Eq. (1.225) is the optical branch and the lower sign the acoustic branch.

At this point we would like to note two additional facts. The Brillouin zone boundary along the [110] direction is the K point and is located at $\vec{k} = \frac{2\pi}{a}(3/4,3/4,0)$. If we continue past the zone boundary to the point $\frac{2\pi}{a}(1,1,0)$, this point is equivalent by symmetry to the X point. The reason for this can be seen by using the properties[48]

$$\omega(\vec{k}+\vec{G},j) = \omega(\vec{k}j) \tag{1.226}$$

$$\omega^2(\overleftrightarrow{S}\cdot\vec{k}j) = \omega^2(\vec{k}j) \tag{1.227}$$

together with the reciprocal lattice vector

$$\vec{G} = \frac{2\pi}{a}(-1,-1,0) \tag{1.228}$$

and the rotation about the X_2 axis

$$\overleftrightarrow{S} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} . \tag{1.229}$$

The $\vec{G}$ vector takes $\frac{2\pi}{a}(1,1,0)$ into $2\pi/a(0,0,1)$. The rotation about the x_2 axis takes $\frac{2\pi}{a}(0,0,1)$ into $\frac{2\pi}{a}(1,0,0)$ which is the X point.

[111] DIRECTION

Along the [111] direction the wavevector $\vec{k}$ is

$$\vec{k} = \frac{k}{\sqrt{3}}(\hat{e}_1+\hat{e}_2+\hat{e}_3) \ . \tag{1.230}$$

Direct computation using the model developed in previous sections allows one to write the dynamical matrix along [111] as

$$[D_{\alpha\beta}(\kappa\kappa'|k)] = \begin{pmatrix} C_1 & C_2 & C_2 & C_3 & C_4 & C_4 \\ C_2 & C_1 & C_1 & C_4 & C_3 & C_4 \\ C_2 & C_2 & C_1 & C_4 & C_4 & C_3 \\ C_3^* & C_4^* & C_4^* & C_1 & C_2 & C_2 \\ C_4^* & C_3^* & C_4^* & C_2 & C_1 & C_2 \\ C_4^* & C_4^* & C_3^* & C_2 & C_2 & C_1 \end{pmatrix} \tag{1.231}$$

where C_1 and C_2 are real and we have defined

$$C_1 = A + D_{11}^{dd}(0,0|k) \tag{1.232a}$$

$$C_2 = B + D_{12}^{dd}(0,0|k) \tag{1.232b}$$

$$C_3 = C + D_{11}^{dd}(0,1|k) \tag{1.232c}$$

$$C_4 = D + D_{12}^{dd}(0,1|k) \tag{1.232d}$$

and

$$A = \frac{1}{M}\begin{bmatrix} 4\alpha+8\mu'+4\lambda'+10\sigma \\ +(8\mu+4\lambda+8\mu''+4\lambda'')\sin^2\frac{ka}{2\sqrt{3}}+\frac{2\sigma}{3}\cos\frac{ka}{\sqrt{3}} \end{bmatrix} \tag{1.233a}$$

$$B = \frac{1}{M}(4\nu+2\sigma/3)\sin^2\frac{ka}{2\sqrt{3}} \qquad (1.233b)$$

$$C = -\frac{1}{M}\begin{bmatrix}(\alpha+8\sigma/3)(1+3e^{-ika/\sqrt{3}}) \\ +(2\mu'+\lambda')(2+e^{-ika/\sqrt{3}}+e^{-2ika/\sqrt{3}}\end{bmatrix} \qquad (1.233c)$$

$$D = \frac{1}{M}\begin{bmatrix}(-\beta+4\sigma/3)(1-e^{-ika/\sqrt{3}})+2\nu'+(2\delta'-\nu')e^{-ika/\sqrt{3}} \\ -(2\delta'+\nu')e^{-2ika/\sqrt{3}}\end{bmatrix} . \qquad (1.233d)$$

Consider first the Λ_1 modes which are longitudinal. Noting that along [111]

$$e^{i\vec{k}\cdot\vec{R}(1)} = e^{\sqrt{3}\,i\,ka/4} \qquad (1.234)$$

we have

$$W_\alpha(0) = b(\delta_{\alpha1}+\delta_{\alpha2}+\delta_{\alpha3}) \qquad (1.235a)$$

$$W_\alpha(1) = e^{\sqrt{3}\,i\,ka/4}\ c(\delta_{\alpha1}+\delta_{\alpha2}+\delta_{\alpha3}) . \qquad (1.235b)$$

Substituting Eqs. (1.235) into Eq. (1.20) and using Eq. (1.231) we obtain the secular equation

$$\omega^2_{\Lambda_1}\pm = (C_1+C_2) \pm [(C_3^*+2C_4^*)(C_3+2C_4)]^{\frac{1}{2}} . \qquad (1.236)$$

At the L point of the Brillouin zone boundary $\vec{k} = \frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and C_3 and C_4 become purely real. We then have

$$\omega^2_{LAL} = \frac{1}{M}\begin{pmatrix} 6\alpha-4\beta+8\mu+8\nu+4\lambda+4\mu'+2\lambda'+4\nu'-8\delta' \\ +\ 8\mu''+4\lambda''+64\sigma/3 \end{pmatrix}$$

$$+\ \frac{4\pi(3p_1-2p_2)^2}{\epsilon M\Omega_o}\left(T^{22}_{11}(L)+V^{22}_{11}(L)\right) \qquad (1.237a)$$

and

$$\omega^2_{LOL} = \frac{1}{M}\begin{pmatrix} 2\alpha+4\beta+8\mu+8\nu+4\lambda+12\mu'+6\lambda'-4\nu'+8\delta' \\ +\ 8\mu''+4\lambda'' \end{pmatrix}$$

$$+\ \frac{4\pi(p_1+2p_2)^2}{\epsilon M\Omega_o}\left(T^{22}_{11}(L)-V^{22}_{11}(L)\right) \qquad (1.237b)$$

where

$$T^{22}_{11}(L) = 2.30147423 \qquad (1.238a)$$

$$V^{22}_{11}(L) = -4.45445881\ . \qquad (1.238b)$$

Note that the dipoles push the LA mode down and the LO mode up.

Now we proceed to the transverse modes. These modes are labeled Λ_3 and are doubly degenerate. One eigenvector is

$$W_\alpha(0) = a(\delta_{\alpha 1}-\delta_{\alpha 2}) \qquad (1.239a)$$

$$W_\alpha(1) = e^{\sqrt{3}\, i\, ka/4}\, b(\delta_{\alpha 1}-\delta_{\alpha 2})\ . \qquad (1.239b)$$

Substituting Eqs. (1.239) into Eq. (1.20) and using Eq. (1.231) we obtain the secular equation

$$\omega^2_{\Lambda_3 \pm} = (C_1 - C_2) \pm \left[(C_3^* - C_4^*)(C_3 - C_4) \right]^{\frac{1}{2}} \; . \qquad (1.240)$$

At the L point we have

$$\omega^2_{TAL} = \frac{1}{M}\begin{pmatrix} 2\alpha - 2\beta + 8\mu - 4\nu + 4\lambda + 12\mu' + 6\lambda' + 2\nu' \\ -4\delta' + 8\mu'' + 4\lambda'' + 6\sigma \end{pmatrix}$$

$$+ \frac{4\pi (p_1 - p_2)^2}{\epsilon M \Omega_o} \left(V^{11}_{12}(L) - T^{11}_{12}(L) \right) \qquad (1.241a)$$

and

$$\omega^2_{TOL} = \frac{1}{M}\begin{pmatrix} 6\alpha + 2\beta + 8\mu - 4\nu + 4\lambda + 4\mu' + 2\lambda' - 2\nu' + 4\delta' \\ + 8\mu'' + 4\lambda'' + 34\sigma/3 \end{pmatrix}$$

$$- \frac{2\pi (3p_1 + p_2)^2}{\epsilon M \Omega_0} \left(T^{22}_{11}(L) + V^{22}_{11}(L) \right) \qquad (1.241b)$$

where

$$T^{11}_{12}(L) = -3.15523204 \qquad (1.242a)$$

$$V^{11}_{12}(L) = -6.53319856 \; . \qquad (1.242b)$$

From Eqs. (1.241) we see that the dipoles push the TA mode down and the TO mode up.

CONDITION OF MINIMUM POTENTIAL ENERGY

Since we have expanded the potential energy about its minimum value, we must insure that this condition holds. The static potential energy Φ_0 can be written as

$$\Phi_0 = \frac{1}{2}(2N)(4\phi_1(r_0) + 12\phi_2(r_2) + 12\phi_3(r_3) + 6\phi_4(a)) , \tag{1.243}$$

where N is the number of unit cells in the crystal. In writing Eq. (1.243) we have noted that the dipole terms give no contribution to the static potential energy, and neither do the angle bending terms. The condition of minimum potential energy requires

$$\frac{\partial \Phi_o}{\partial r_o} = 0 . \tag{1.244}$$

Using Eqs. (1.9), (1.69), (1.81), (1.89) and (1.98) we obtain

$$\alpha - \beta + 8\mu - 8\nu + 11\mu' - 11\nu' + 8\mu'' = 0 , \tag{1.245a}$$

or

$$\left[\frac{\phi_1'(r_0)}{r_0} + \frac{8\phi_2'(r_2)}{r_2} + \frac{11\phi_3'(r_3)}{r_3} + \frac{8\phi_4'(a)}{a}\right] = 0 . \tag{1.245b}$$

Eqs. (1.245) give a relation between the force constant parameters that must be satisfied for our model. Note that this condition is trivially satisfied if all first order potential derivatives are zero.

PHONON DISPERSION CURVES AND FITS TO EXPERIMENTAL DATA FOR SILICON

In this section we present two basic models. First we examine a four parameter model that illustrates the effect of the dipoles on the phonon dispersion curves. Second we present a fit to experimental data using a ten parameter model.

FOUR PARAMETER MODEL

This was the first model used when investigating the effect of the dipoles on the phonon dispersion curves. In this model we take as parameters $\alpha = \beta$, $\mu = \nu$, σ and p_1 , with all other parameters zero. This corresponds to purely central force first and second neighbor interactions, angle bending and what we will call diagonal nonlocal dipoles, since the matrices Eq. (1.150) are diagonal for this case. The experimental data[49] fit are C_{11}, C_{12}, ω_{RA} and ω_{TAX} . The parameters determined in this manner are given in Table 2. An interesting feature of this model is that the short-range force constants are completely determined by C_{11}, C_{12} and ω_{RA} . The single dipole parameter is determined by ω_{TAX} . Since the dipole interaction does not affect C_{11}, C_{12}, C_{44} and ω_{RA} , a comparison of this model to one using the same short-range force constants but no dipoles can be made.

Table 2 - Four Parameter Dipole Model. The experimental values of C_{11}, C_{12}, ω_{RA} and ω_{TAX} have been used to determine the parameters. $p_1 = z_1 e$ where e is the magnitude of the electron charge in C.G.S. units.

$$\alpha = \beta = 3.672 \times 10^4 \text{dyne/cm}$$
$$\mu = \nu = 3.080 \times 10^3 \text{dyne/cm}$$
$$\sigma = 7.163 \times 10^3 \text{dyne/cm}$$
$$z_1 = 0.8518$$

$$\phi_1''(r_0) = 1.102 \times 10^5 \text{dyne/cm}$$
$$\phi_2''(r_2) = 6.161 \times 10^3 \text{dyne/cm}$$

Calculated value of C_{44}

$$C_{44} = 7.476 \times 10^{11} \text{dyne/cm}^2$$

Experimental value of C_{44}

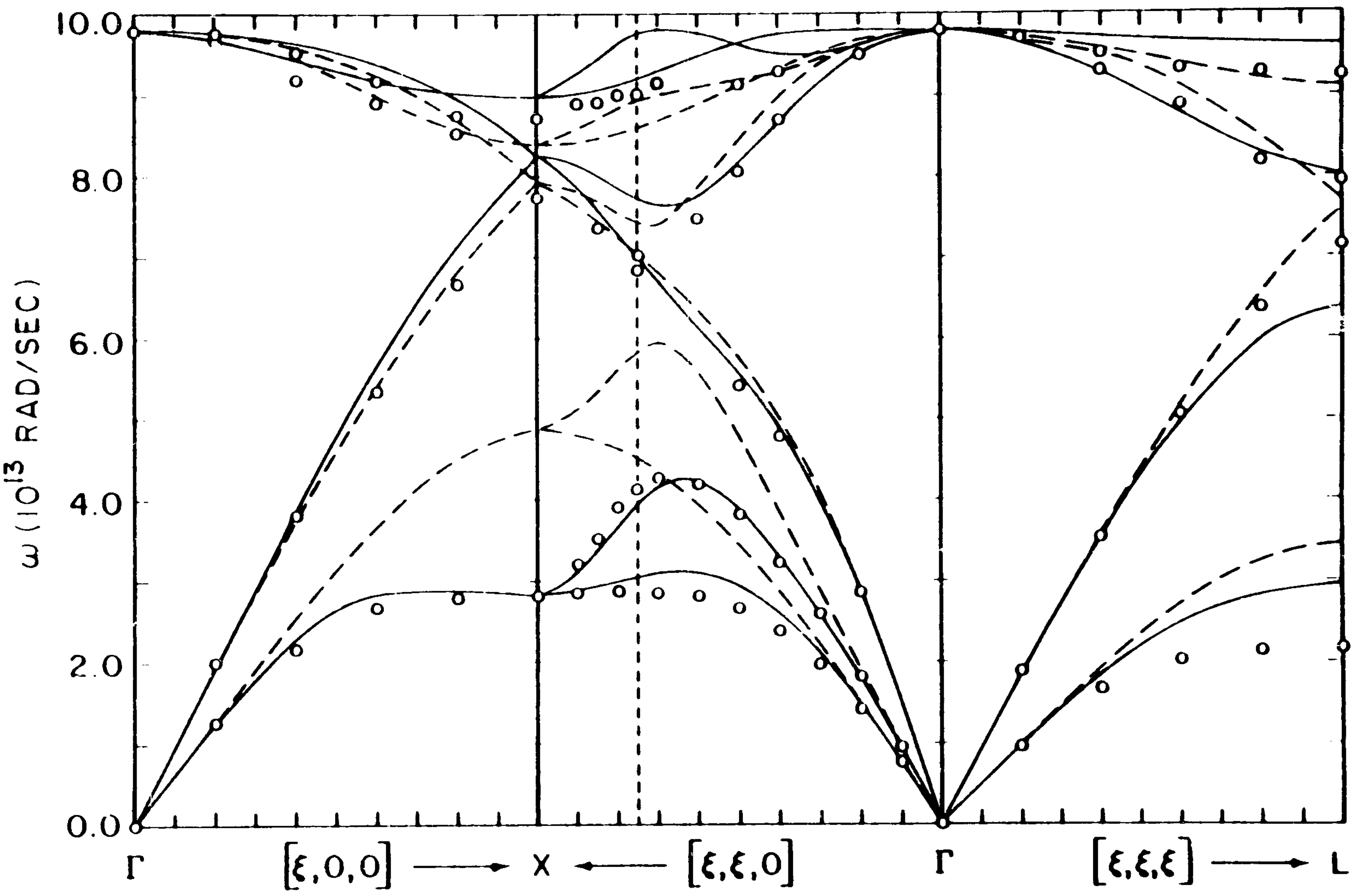
$$C_{44} = 7.963 \times 10^{11} \text{dyne/cm}^2$$

In Fig. 8 we have plotted the phonon dispersion curves along symmetry directions for the four parameter dipole model. Also plotted for comparison are the dispersion curves for the same short-range force constants but no dipoles. Note the dramatic lowering of the TA modes near the zone boundaries along the [100] and [110] directions due to the dipoles. The TA [111] modes are also lowered, but not nearly as much as the [100] modes. The major feature of the dipole model is that it allows lowering of the TA modes while maintaining a high value of C_{44} . (Note that the calculated value of C_{44} in this model is within 6% of the experimental value.)

Although the dipoles improve agreement with experiment, the basic shortcoming of them is that the TAX modes are lowered much more than the TAL modes. This is a problem with the angular variation of the dipoles which is not remedied by addition of the nondiagonal parameter p_2 , since the quantity (p_1-p_2) enters into both Eq. (1.200) and Eq. (1.241a). It is possible that extending the dipole model to second neighbor nonlocality could remedy this deficiency.

From the expressions given by Lax[50] we see that his quadrupoles tend to restore the balance between the TAX and TAL lowering. However the quadrupoles also affect the elastic constants and Raman frequency. It is the opinion of this author that including dipole-quadrupole and quadrupole-quadrupole interactions would remedy the shortcoming of the angular variation of the dipoles. This could be done with the addition of only one more parameter for the quadrupoles, as in the work of Lax. The dipole-quadrupole interaction should be interesting since it is a mixture of nonlocal dipoles with local quadrupoles. The difficulty with this approach is application of the Ewald method twice more for the long-range sums.

Figure 8. Four parameter dipole model as described in the text (solid lines). Circles are experimental data (Ref. 49). The dashed lines are the same short-range force constants but with no dipoles.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8.0
6.0
4.0
2.0
0.0
Γ
[ξ,0,0] ⟶ X ⟵ [ξ,ξ,0]
Γ
[ξ,ξ,ξ] ⟶ L

TEN PARAMETER MODEL

In an attempt to improve the four parameter dipole model of the previous section, we have included third and fourth neighbor central potential interactions and the non-diagonal dipole parameter p_2. The first derivatives of the potentials are also allowed to be nonzero, subject only to the condition Eq. (1.245b). The ten independent parameters are $\phi_1''(r_0)$, $\phi_2''(r_2)$, $\phi_3''(r_3)$, $\phi_4''(a)$, $\phi_1'(r_0)$, $\phi_2'(r_2)$, $\phi_3'(r_3)$, σ, p_1 and p_2. ($\phi_4'(a)$ is determined by Eq. (1.245b)). The parameters were determined in the following manner. Using the analytic expressions for $M\omega_{RA}^2$, aC_{11}, aC_{12}, $M\omega_{LAX}^2$, $M\omega_{TAX}^2$, $M\omega_{TOX}^2$, $M\omega_{TAL}^2$, $M\omega_{LAL}^2$, $M\omega_{LOL}^2$, $M\omega_{TOL}^2$, and aC_{44} we performed a nine parameter, weighted, nonlinear least square fit to the experimental values of these quantities for a given assumed ratio of p_2/p_1. The ratio p_2/p_1 was then varied to obtain best agreement with the Σ_3 mode near the K point consistent with the smallest value of least squares of the above quantities.

The method of solution of the set of nonlinear equations is the Newton Raphson iteration with the zero-order parameter values determined from a linear least square fit to all the preceding experimental quantities except C_{44}. A typical nonlinear fit converges to an accuracy of ten decimals in ten iterations, the value of C_{44} changing by almost a factor of two from the value computed using the zero-order parameters.

The entire fitting procedure is made somewhat subjective by the weighting factors which are necessary to obtain a reasonable fit to the data. These weights had to be input by hand using the trial and error method and the criterion that the percent errors in the frequencies be nearly the same. Obtaining such fits to the data is tedious and time consuming at best.

In spite of the above mentioned difficulties, we have obtained a reasonably accurate fit to the neutron scattering data plus elastic constants. The parameters for this fit are given in Table 3. In Table 4 we list the potential derivatives for this fit. Note the rapid fall off of the potential derivatives by the fourth neighbor distance. The dispersion curves for the model with these parameter values are plotted in Fig. 9. The model reproduces the low-lying acoustic modes rather well and the elastic constants are within 13% of the experimental values. Though this is not stunning, it is a marked improvement over models employing only first thru fifth neighbor interactions of the type used in this thesis. The parameters in Table 3 should not be taken as the best fit possible with the ten parameter model since the author has not exhausted all the regions of parameter space in combination with all possible weights in the fitting procedure.

Table 3 - Ten Parameter Dipole Model. $p_1 = z_1 e$ and $p_2 = z_2 e$ where e is the magnitude of the electron charge in C.G.S. units.

$\alpha = 4.7008 \times 10^4$ dyne/cm

$\beta = 3.0364 \times 10^4$

$\mu = 5.4455 \times 10^3$

$\nu = 4.7303 \times 10^3$

$\lambda = (\mu - \nu) = 7.1520 \times 10^2$

$\sigma = 4.3265 \times 10^3$

$\mu' = -2.2679 \times 10^3$

$\nu' = -8.0545 \times 10$

$\lambda' = (\mu' + 8\nu') = -2.9122 \times 10^3$

$\delta' = 3\nu' = -2.4164 \times 10^2$

$\lambda'' = 9.9978 \times 10$

$\mu'' = -\frac{1}{8}(\alpha - \beta + 8\mu - 8\nu + 11\mu' - 11\nu') = 2.1190 \times 10^2$

$z_1 = 0.804905$ $z_2 = -0.201226$ $z_2/z_1 = -0.25$

Elastic Constants

	Calculated	Experimental*
C_{11}	1.4352×10^{12} dyne/cm^2	1.6578×10^{12}
C_{12}	7.2011×10^{11}	6.3937×10^{11}
C_{44}	7.0152×10^{11}	7.9625×10^{11}

*(McSkimin, ref. 49)

<u>Table 4</u> - Potential Derivatives for the Ten Parameter Dipole Model.

$$\phi_1''(r_0) = (\alpha+2\beta) = 1.0774 \times 10^5 \text{dyne/cm}$$

$$\frac{\phi_1'(r_0)}{r_0} = (\alpha-\beta) = 1.6644 \times 10^4$$

$$\phi_2''(r_2) = (\mu+\nu) = 1.0176 \times 10^4$$

$$\frac{\phi_2'(r_2)}{r_2} = \lambda = 7.1520 \times 10^2$$

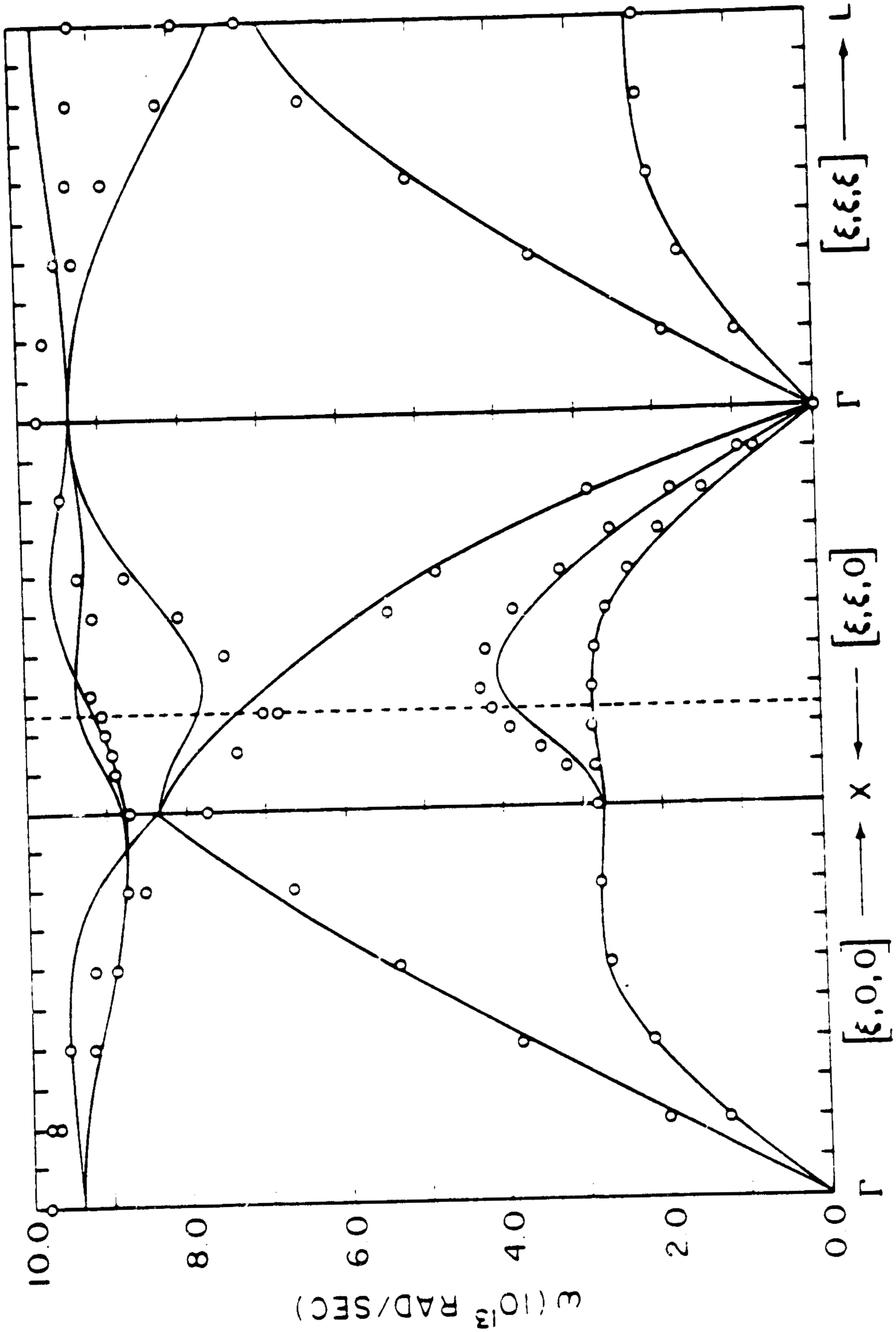
$$\phi_3''(r_3) = (\mu'+10\nu') = -3.073 \times 10^3$$

$$\frac{\phi_3'(r_3)}{r_3} = (\mu'-\nu') = -2.1873 \times 10^3$$

$$\phi_4''(a) = \lambda'' = 9.9978 \times 10$$

$$\frac{\phi_4'(a)}{a} = \mu'' = 2.1190 \times 10^2$$

Figure 9. Ten parameter dipole model as described in the text (solid lines). Circles are experimental data (Ref. 49).


ω (10^{13} RAD/SEC)
10.0
8.0
6.0
4.0
2.0
0.0
Γ
[ε,0,0]
X
[ε,ε,0]
Γ
[ε,ε,ε]
L

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Chapter 2

Thermal Expansion of the Diamond Structure

> "For what is a man profited, if he
> shall gain the whole world, and
> lose his own soul? or what shall
> a man give in exchange for his
> soul?"
>
> Matthew 16:26

INTRODUCTION

In this chapter we focus on aspects of the anharmonic lattice dynamics of the diamond structure that are necessary to calculate the thermal expansion. First we review some relevant thermodynamic formulas and then develop the statistical mechanics treatment of thermal expansion to lowest order in the anharmonicity. Next we present an anharmonic model which is a consistent extension of the harmonic model of Chapter 1. In the process of developing this model we found analytic expressions that explain in a simple way how the negative Grüneisen parameters arise. Analytic expressions for the mode Grüneisen parameters for several modes are presented. A fit to the experimental data available for silicon is made and dispersion curves for the mode gammas along symmetry directions are presented. The model is then used to calculate the volume thermal expansion coefficient of silicon between 5 and 1700K. Also calculated are the thermal strain, zero-point strain and zero-point phonon pressure.

THERMODYNAMICS REVIEW

The purpose of this section is to define some thermodynamic quantities and derive some formulas that are useful in connection with thermal expansion. We begin with the Helmholtz free energy for the crystal[1]

$$F(T,V) = E-TS \; , \tag{2.1}$$

where T is the temperature, V the volume, E the internal energy and S the entropy of the crystal. Taking the total derivative of Eq. (2.1) we find

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV = dE - TdS - SdT \; . \tag{2.2}$$

Using the fact that for a reversible process[2]

$$TdS = dE + PdV \; , \tag{2.3}$$

where P is the pressure, we obtain from Eq. (2.2) that

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \; , \tag{2.4a}$$

and

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \; . \tag{2.4b}$$

Equation (2.4a) is the equation of state since it relates the pressure to the temperature and volume. Note that if the pressure is zero, then the crystal volume is determined from Eq. (2.4a) by setting to zero the derivative of the Helmholtz free energy with respect to volume.

The volume expansion coefficient is defined as[3]

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad . \tag{2.5}$$

Since[4]

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V , \tag{2.6}$$

we have upon using Eqs. (2.4a) and (2.6) that

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V \quad . \tag{2.7}$$

Using the definition of the isothermal bulk modulus[5]

$$B = - V\left(\frac{\partial P}{\partial V}\right)_T , \tag{2.8}$$

we obtain using Eq. (2.4a) that

$$B = V\left(\frac{\partial^2 F}{\partial V^2}\right)_T \quad . \tag{2.9}$$

Furthermore, since

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T^{-1} , \tag{2 10}$$

we have that

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{B}, \qquad (2.11)$$

so that Eq. (2.7) becomes

$$\alpha = -\frac{1}{B}\left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V . \qquad (2.12)$$

Note that the order of differentiation is interchangeable in Eq. (2.12). Equations (2.4a), (2.9) and (2.12) clearly show the central role of the Helmholtz free energy.

STATISTICAL MECHANICS TREATMENT

The Helmholtz free energy is given in terms of the partition function Z by[6]

$$F = - k_B T \ln Z \tag{2.13}$$

where[7]

$$Z = \mathrm{Tr}\, e^{-\beta H} . \tag{2.14}$$

The trace in Eq. (2.14) is over a complete set of states, k_B is Boltzmann's constant, $\beta = 1/k_B T$ and H is the Hamiltonian of the system. For our purpose here, we consider the Hamiltonian

$$H = T + \Phi , \tag{2.15}$$

with T the kinetic energy given by Eq. (1.15) and Φ the potential energy as a function of nuclear displacements. Expanding about the configuration of minimum potential energy we have

$$\begin{aligned} \Phi = {} & \Phi_o(V_o) + \frac{1}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')u_\alpha(\ell\kappa)u_\beta(\ell'\kappa') \\ & + \frac{1}{6} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta \\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')u_\alpha(\ell\kappa)u_\beta(\ell'\kappa')u_\gamma(\ell''\kappa'') \\ & + \cdots . \end{aligned} \tag{2.16}$$

Here V_o denotes the volume of the configuration of minimum potential energy, $\Phi_o(V_o)$ the static potential energy of this configuration, the second order force constants are defined by Eq. (1.17) and the third order force constants are defined by

$$\Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \left.\frac{\partial^3\Phi}{\partial u_\alpha(\ell\kappa)\partial u_\beta(\ell'\kappa')\partial u_\gamma(\ell''\kappa'')}\right|_o \quad . \tag{2.17}$$

In Eq. (2.16) we have only kept cubic anharmonic terms. This is sufficient for calculation of the thermal expansion to lowest order in the anharmonicity.

In what follows, we will term the "bare" crystal as the crystal oscillating about the configuration of minimum potential energy, characterized by the position vectors Eq. (1.5). As we shall see, this is not the physical crystal since the presence of anharmonicity causes a finite strain even at the absolute zero of temperature.

Now consider an isotropic homogeneous deformation of the crystal. We define new dynamic displacements $v_\alpha(\ell\kappa)$ by the equation

$$u_\alpha(\ell\kappa) = \epsilon R_\alpha(\ell\kappa) + v_\alpha(\ell\kappa) \ , \tag{2.18}$$

where ϵ is the deformation parameter or strain. The new position vectors of the deformed lattice are

$$\tilde{R}_{\alpha}(\ell\kappa) = (1+\epsilon)R_{\alpha}(\ell\kappa) \ , \tag{2.19}$$

so that the volume of the deformed crystal is

$$V = (1+\epsilon)^{3}V_{o} \ . \tag{2.20}$$

Substituting Eq. (2.18) into Eq. (2.16) we obtain for the potential energy

$$\Phi = \tilde{\Phi}_{0} + \tilde{\Phi}_{1} + \tilde{\Phi}_{2} + \tilde{\Phi}_{3} \ , \tag{2.21}$$

with

$$\tilde{\Phi}_{0} = \Phi_{0}(V_{o}) + \frac{\epsilon^{2}}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')R_{\alpha}(\ell\kappa)R_{\beta}(\ell'\kappa')$$
$$+ \frac{\epsilon^{3}}{6} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta \\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_{\alpha}(\ell\kappa)R_{\beta}(\ell'\kappa')R_{\gamma}(\ell''\kappa'') \ , \tag{2.22a}$$

$$\tilde{\Phi}_{1} = \epsilon \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')R_{\alpha}(\ell\kappa)v_{\beta}(\ell'\kappa')$$
$$+ \frac{\epsilon^{2}}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta \\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_{\alpha}(\ell\kappa)R_{\beta}(\ell'\kappa')v_{\gamma}(\ell''\kappa''), \tag{2.22b}$$

$$\tilde{\Phi}_2 = \frac{1}{2} \sum_{\substack{\ell\kappa\alpha\\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')v_\alpha(\ell\kappa)v_\beta(\ell'\kappa')$$

$$+ \frac{\epsilon}{2} \sum_{\substack{\ell\kappa\alpha\\ \ell'\kappa'\beta\\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_\alpha(\ell\kappa)v_\beta(\ell'\kappa')v_\gamma(\ell''\kappa'') , \tag{2.22c}$$

and

$$\tilde{\Phi}_3 = \frac{1}{6} \sum_{\substack{\ell\kappa\alpha\\ \ell'\kappa'\beta\\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')v_\alpha(\ell\kappa)v_\beta(\ell'\kappa')v_\gamma(\ell''\kappa'') . \tag{2.22d}$$

We further define the perturbations to the static lattice energy and force constants as

$$\Phi_0^{(2)} = \frac{1}{2} \sum_{\substack{\ell\kappa\alpha\\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')R_\alpha(\ell\kappa)R_\beta(\ell'\kappa') , \tag{2.23a}$$

$$\Phi_0^{(3)} = \frac{1}{6} \sum_{\substack{\ell\kappa\alpha\\ \ell'\kappa'\beta\\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_\alpha(\ell\kappa)R_\beta(\ell'\kappa')R_\gamma(\ell''\kappa'') , \tag{2.23b}$$

$$\Phi_\alpha^{(1)}(\ell\kappa) = \sum_{\ell'\kappa'\beta} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')R_\beta(\ell'\kappa') , \tag{2.23c}$$

$$\Phi_\alpha^{(2)}(\ell\kappa) = \frac{1}{2} \sum_{\substack{\ell'\kappa'\beta\\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_\beta(\ell'\kappa')R_\gamma(\ell''\kappa'') , \tag{2.23d}$$

$$\Phi_{\alpha\beta}^{(1)}(\ell\kappa|\ell'\kappa') = \sum_{\ell''\kappa''\gamma} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_\gamma(\ell''\kappa'') . \tag{2.23e}$$

Since the deformation is isotropic, the perturbations to the force constants will have the same symmetry properties as the respective force constants of the same order. This being the case, we have for the diamond structure that

$$\Phi_{\alpha}^{(1)}(\ell\kappa) = 0 \tag{2.24a}$$

and

$$\Phi_{\alpha}^{(2)}(\ell\kappa) = 0 \ , \tag{2.24b}$$

so that

$$\tilde{\Phi}_1 = 0 \ . \tag{2.24c}$$

Equations (2.24) are shown in Appendix F. Thus we can rewrite the potential energy as

$$\Phi = \tilde{\Phi}_0 + \frac{1}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} [\Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') + \epsilon\Phi_{\alpha\beta}^{(1)}(\ell\kappa|\ell'\kappa')] v_{\alpha}(\ell\kappa) v_{\beta}(\ell'\kappa')$$

$$+ \frac{1}{6} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta \\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') v_{\alpha}(\ell\kappa) v_{\beta}(\ell'\kappa') v_{\gamma}(\ell''\kappa'') \ . \tag{2.25}$$

Writing the Hamiltonian as

$$H = H_0 + H_1 \ , \tag{2.26}$$

with

$$H_0 = T + \Phi_0(V_o) + \frac{1}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') v_\alpha(\ell\kappa) v_\beta(\ell'\kappa') \ , \tag{2.27a}$$

and

$$H_1 = \epsilon^2 \Phi_0^{(2)} + \epsilon^3 \Phi_0^{(3)} + \frac{\epsilon}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}^{(1)}(\ell\kappa|\ell'\kappa') v_\alpha(\ell\kappa) v_\beta(\ell'\kappa')$$
$$+ \frac{1}{6} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta \\ \ell''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') v_\alpha(\ell\kappa) v_\beta(\ell'\kappa') v_\gamma(\ell''\kappa'') \ , \tag{2.27b}$$

we see that H_0 is the Hamiltonian of the bare harmonic crystal in terms of the displacements $v_\alpha(\ell\kappa)$, and H_1 contains the anharmonic effects. Note that all the strain dependence is contained in the H_1 term. To lowest order in H_1 the Helmholtz free energy is given by[8]

$$F = F_0 + \langle H_1 \rangle_0 \ , \tag{2.28}$$

where for any operator M

$$\langle M \rangle_0 = \frac{1}{Z_0} \mathrm{Tr}\left(e^{-\beta H_0} M\right), \tag{2.29}$$

$$F_0 = -\frac{1}{\beta} \ln Z_0 \ , \tag{2.30}$$

and

$$Z_0 = \mathrm{Tr}\, e^{-\beta H_0} . \tag{2.31}$$

Using Eq. (2.27b) we obtain

$$\langle H_1\rangle_0 = \epsilon^2 \Phi_0^{(2)} + \epsilon^3 \Phi_0^{(3)} + \frac{\epsilon}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}^{(1)}(\ell\kappa|\ell'\kappa') \times$$

$$\times \langle v_\alpha(\ell\kappa) v_\beta(\ell'\kappa')\rangle_0 , \tag{2.32}$$

where we have used the fact that[9]

$$\langle v_\alpha(\ell\kappa) v_\beta(\ell'\kappa') v_\gamma(\ell''\kappa'')\rangle_0 = 0 . \tag{2.33}$$

Consider next the normal coordinate transformation[10]

$$v_\alpha(\ell\kappa) = \sum_{\vec{k}j}^{BZ} \left(\frac{\hbar}{2NM\omega(\vec{k}j)}\right)^{\frac{1}{2}} e_\alpha(\kappa|\vec{k}j) e^{i\vec{k}\cdot\vec{R}(\ell)} A_{\vec{k}j} , \tag{2.34}$$

where $A_{\vec{k}j}$ is the phonon field operator given in terms of the usual creation and destruction operators by

$$A_{\vec{k}j} = b_{\vec{k}j} + b^\dagger_{-\vec{k}j} . \tag{2.35}$$

The BZ on top of the sum in Eq. (2.34) is a reminder that the sum is restricted to the first Brillouin zone and N is the number of unit cells in the crystal. We also have the expectation value[11]

$$\langle A_{\vec{k}j} A_{\vec{k}'j'}\rangle_0 = \delta_{\vec{k},-\vec{k}'} \delta_{jj'} (2\bar{n}_{\vec{k}j} + 1) , \tag{2.36}$$

where

$$\bar{n}_{\vec{k}j} = (e^{\beta\hbar\omega(\vec{k}j)} - 1)^{-1} \ . \qquad (2.37)$$

Using Eqs. (2.34) and (2.36) we obtain

$$\langle v_\alpha(\ell\kappa)v_\beta(\ell'\kappa')\rangle_0 = \sum_{\vec{k}j}^{BZ} \frac{\hbar}{2NM\omega(\vec{k}j)} e^*_\alpha(\kappa|\vec{k}j)e_\beta(\kappa'|\vec{k}j) \times$$

$$\times\ e^{i\vec{k}\cdot(\vec{R}(\ell')-\vec{R}(\ell))}(2\bar{n}_{\vec{k}j}+1) \ . \qquad (2.38)$$

Substituting Eq. (2.38) into Eq. (2.32) yields

$$\langle H_1\rangle_0 = \epsilon^2\Phi_0^{(2)} + \epsilon^3\Phi_0^{(3)}$$

$$+ \frac{\epsilon\hbar}{4NM}\sum_{\vec{k}j}^{BZ}\ \sum_{\substack{\ell\kappa\alpha\\ \ell'\kappa'\beta}} \frac{(2\bar{n}_{\vec{k}j}+1)}{\omega(\vec{k}j)} e^*_\alpha(\kappa|\vec{k}j)e_\beta(\kappa'|\vec{k}j) \times$$

$$\times\ \Phi^{(1)}_{\alpha\beta}(\ell\kappa|\ell'\kappa')e^{i\vec{k}\cdot(\vec{R}(\ell')-\vec{R}(\ell))} \ . \qquad (2.39)$$

Now we note that

$$\sum_{\ell\ell'}\Phi^{(1)}_{\alpha\beta}(\ell\kappa|\ell'\kappa')e^{i\vec{k}\cdot(\vec{R}(\ell')-\vec{R}(\ell))} = NM\ D^{(1)}_{\alpha\beta}(\kappa\kappa'|\vec{k}) \ , \qquad (2.40)$$

where we have defined the perturbation to the dynamical matrix in analogy with Eq. (1.25),

$$D^{(1)}_{\alpha\beta}(\kappa\kappa'|\vec{k}) = \frac{1}{M}\sum_m \Phi^{(1)}_{\alpha\beta}(0\kappa|m\kappa')e^{i\vec{k}\cdot\vec{R}(m)} \ . \qquad (2.41)$$

Thus Eq. (2.39) becomes

$$\langle H_1\rangle_0 = \epsilon^2\Phi_0^{(2)} + \epsilon^3\Phi_0^{(3)} + \frac{\epsilon\hbar}{4}\sum_{\vec{k}j}^{BZ}\sum_{\substack{\kappa\alpha\\ \kappa'\beta}}\frac{(2\bar{n}_{\vec{k}j}+1)}{\omega(\vec{k}j)}\, e_\alpha^*(\kappa|\vec{k}j)D_{\alpha\beta}^{(1)}(\kappa\kappa'|\vec{k})e_\beta(\kappa'|\vec{k}j)\ . \tag{2.42}$$

Defining

$$\omega_1^2(\vec{k}j) = \sum_{\substack{\kappa\alpha\\ \kappa'\beta}} e_\alpha^*(\kappa|\vec{k}j)D_{\alpha\beta}^{(1)}(\kappa\kappa'|\vec{k})e_\beta(\kappa'|\vec{k}j)\ , \tag{2.43}$$

we have in more compact form

$$\langle H_1\rangle_0 = \epsilon^2\Phi_0^{(2)} + \epsilon^3\Phi_0^{(3)} + \frac{\epsilon\hbar}{2}\sum_{\vec{k}j}^{BZ}\frac{\omega_1^2(\vec{k}j)}{\omega(\vec{k}j)}(\bar{n}_{\vec{k}j}+\tfrac{1}{2})\ . \tag{2.44}$$

Since H_0 does not depend on the strain, to lowest order in H_1 we have from Eq. (2.28) that

$$\frac{\partial F}{\partial\epsilon} = \frac{\partial\langle H_1\rangle_0}{\partial\epsilon}\ , \tag{2.45}$$

so that

$$\frac{\partial F}{\partial\epsilon} = 2\epsilon\Phi_0^{(2)} + 3\epsilon^2\Phi_0^{(3)} + \frac{\hbar}{2}\sum_{\vec{k}j}^{BZ}\frac{\omega_1^2(\vec{k}j)}{\omega(\vec{k}j)}(\bar{n}_{\vec{k}j}+\tfrac{1}{2})\ . \tag{2.46}$$

To proceed to volume derivatives we use Eq. (2.20) so that

$$\frac{\partial F}{\partial V} = \frac{1}{3V_0(1+\epsilon)^2}\,\frac{\partial F}{\partial \epsilon}\ . \tag{2.47}$$

Using Eq. (2.4a) we obtain

$$P = -\frac{1}{3V_0(1+\epsilon)^2}\left[2\epsilon\Phi_0^{(2)}+3\epsilon^2\Phi_0^{(3)}+\frac{\hbar}{2}\sum_{\vec{k}j}^{BZ}\frac{\omega_1^2(\vec{k}j)}{\omega(\vec{k}j)}(\bar{n}_{\vec{k}j}+\tfrac{1}{2})\right]\ . \tag{2.48}$$

From Eq. (2.9) the bulk modulus of the bare crystal in the harmonic approximation is given by

$$B_0 = \frac{2\Phi_0^{(2)}}{9V_0}\ , \tag{2.49}$$

so that to lowest order in ϵ the equation of state is

$$P = 3B_0\epsilon - \frac{\hbar}{6V_0}\sum_{\vec{k}j}^{BZ}\frac{\omega_1^2(\vec{k}j)}{\omega(\vec{k}j)}(\bar{n}_{\vec{k}j}+\tfrac{1}{2})\ . \tag{2.50}$$

Defining the mode Grüneisen parameter by

$$\gamma(\vec{k}j) = -\frac{\omega_1^2(\vec{k}j)}{6\omega^2(\vec{k}j)}\ , \tag{2.51}$$

we have

$$P = -3B_0\epsilon + \frac{\hbar}{V_0}\sum_{\vec{k}j}^{BZ}\omega(\vec{k}j)\gamma(\vec{k}j)(\bar{n}_{\vec{k}j}+\tfrac{1}{2})\ . \tag{2.52}$$

From Eq. (2.52) we see that even at the absolute zero of temperature and zero pressure there is a zero-point strain given by

$$\epsilon_0 = \frac{1}{3B_0V_0} \sum_{\vec{k}j}^{BZ} \frac{\hbar\omega(\vec{k}j)}{2} \gamma(\vec{k}j) \ . \tag{2.53}$$

This can be thought of in terms of the pressure required to make the strain zero at $T = 0$,

$$P_0 = \frac{1}{V_0} \sum_{\vec{k}j}^{BZ} \frac{\hbar\omega(\vec{k}j)}{2} \gamma(\vec{k}j) \ . \tag{2.54}$$

P_0 is thus a zero-point phonon pressure.

Proceeding now to the thermal expansion coefficient, we have from Eqs. (2.12) and (2.47) that

$$\alpha = - \frac{1}{3BV_0(1+\epsilon)^2} \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial \epsilon}\right)_T\right]_\epsilon \ , \tag{2.55}$$

or using Eq. (2.46)

$$\alpha = - \frac{\hbar}{6BV_0(1+\epsilon)^2} \sum_{\vec{k}j}^{BZ} \frac{\omega_1^2(\vec{k}j)}{\omega(\vec{k}j)} \frac{\partial}{\partial T}(\bar{n}_{\vec{k}j} + \tfrac{1}{2}) \ . \tag{2.56}$$

Now

$$\frac{\partial}{\partial T}(\bar{n}_{\vec{k}j} + \tfrac{1}{2}) = \frac{\hbar\omega(\vec{k}j)}{4k_BT^2} \left\{\sinh\left[\frac{\beta\hbar\omega(\vec{k}j)}{2}\right]\right\}^{-2} . \tag{2.57}$$

Defining the Einstein specific heat function as

$$C_E(\omega) = k_B\left(\frac{\beta\hbar\omega}{2}\right)^2 \left\{\sinh[\beta\hbar\omega/2]\right\}^{-2} \ , \tag{2.58}$$

Eq. (2.56) becomes with the aid of Eq. (2.51) to lowest order in ϵ

$$\alpha = \frac{1}{BV_0} \sum_{\vec{k}j}^{BZ} \gamma(\vec{k}j) C_E(\omega(\vec{k}j)) \quad . \tag{2.59}$$

Eq. (2.59) is the same as the result of the "quasi-harmonic" approximation,[12] at least to lowest order in ϵ . This approximation is useful to find the meaning of the mode Grüneisen parameters. In the quasi-harmonic approximation, the phonon frequencies are given to lowest order in ϵ by

$$\tilde{\omega}^2(\vec{k}j) = \omega^2(\vec{k}j) + \epsilon\omega_1^2(\vec{k}j) + \cdots , \tag{2.60}$$

with $\omega_1(\vec{k}j)$ defined by Eq. (2.43). To make connection with experiment, one defines the mode gamma by

$$\gamma(\vec{k}j) = -\frac{d\,\ell n\,\tilde{\omega}(\vec{k}j)}{d\,\ell n\,V} \tag{2.60}$$

or

$$\gamma(\vec{k}j) = -\frac{V}{2\tilde{\omega}^2(\vec{k}j)} \frac{d\tilde{\omega}^2(\vec{k}j)}{dV} \quad . \tag{2.61}$$

Using Eqs. (2.20) and (2.60) we obtain

$$\gamma(\vec{k}j) = -\frac{(1+\epsilon)}{6\tilde{\omega}^2(\vec{k}j)} \omega_1^2(\vec{k}j) , \tag{2.62}$$

so that to lowest order in ϵ

$$\gamma(\vec{k}j) = -\frac{\omega_1^2(\vec{k}j)}{6\omega^2(\vec{k}j)} . \tag{2.63}$$

Equation (2.63) agrees with the definition Eq. (2.51). To proceed one step further, experiments measure the pressure dependence of phonon frequencies for some modes and thus one can obtain experimental information about the mode gammas.

ANHARMONIC MODEL

In order to calculate the thermal expansion using Eq. (2.59), it is necessary to have a model for the mode gammas. The earliest model of Grüneisen[13] was to assume that $\gamma(\vec{k}j)$ was a constant, the same for each mode, and thus the thermal expansion would have essentially the same temperature dependence as the specific heat. This is known as Grüneisen's rule. It is a reasonable approximation for some materials, but since the specific heat and bulk modulus are always positive, it is completely inadequate to describe materials with negative thermal expansion that have a change in sign of the expansion coefficient.

It is interesting to note that a linear monatomic chain of atoms with nearest neighbor interactions gives a mode gamma that is the same for each mode.[14] Thus we have one example where Grüneisen's rule is rigorously justified. However, the inclusion of second neighbor interactions introduces dispersion so that the mode gammas become wavelength dependent even in this simple, one-dimensional model.[15]

Several discussions of negative thermal expansion have appeared in the literature. Experimentally, negative thermal expansion has been observed in the tetrahedrally bonded solids[16] C, Si, Ge, GaAs, GaSb, CdSe, CdS, CdTe, AgI, InSb, CuCℓ, CuF, CuI, HgTe, ZnO, ZnSe, ZnS, ZnTe, hexagonal ice and $CuInTe_2$. Negative thermal expansion has also been observed in the tetrahedral glasses SiO_2 , GeO_2 , BeF_2 and $SiO_2 + x\%Na_2O$ for x less than 0.2 . Negative thermal expansion also occurs in other crystal structures (fcc RbBr and RbI , for example) but is relatively rare in comparison with the tetrahedral solids.

On the theoretical side, the occurence of negative thermal expansion may be understood from Eq. (2.59) if the mode Grüneisen parameters are negative for enough modes that contribute a large weight to the sum in Eq. (2.59). Although several discussions of negative Grüneisen parameters have appeared in the literature, none of them have been very realistic or explicit in explaining how the negative mode gammas arise. For this reason we use a model with sufficient generality to explain the origin of the negative Grüneisen parameters and present analytic expressions for them for several modes.

The anharmonic model we use is a consistent extension of the harmonic model developed in Chapter 1. The reason for mentioning this is because previous calculations for silicon[17] have used a shell model for the harmonic properties and a rigid ion model for the anharmonic properties, with no relation between the two. In fact, the first and second order potential derivatives which enter the harmonic model also strongly affect the anharmonic model, as we shall see.

In order to compute the mode Grüneisen parameters, once we have the harmonic and anharmonic models, we only need compute the perturbation to the dynamical matrix Eqs. (2.41) and (2.23e). Since the perturbations to the force constants have the same symmetry properties as the second order force constants, once we have obtained the form of the dynamical matrix for the harmonic model, the form of the perturbation to the dynamical matrix can be written down immediately. The actual values of the perturbations must be calculated from physical considerations.

CENTRAL POTENTIAL CONTRIBUTIONS

For two body central potential interactions we can write the cubic anharmonic contribution to the potential energy as

$$\Phi_{3C} = \frac{1}{12} \sum_{\ell\kappa} \sum_{\ell'\kappa'} \sum_{\alpha\beta\gamma} \phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa') u_\alpha(\ell\kappa|\ell'\kappa') \times$$

$$\times\, u_\beta(\ell\kappa|\ell'\kappa') u_\gamma(\ell\kappa|\ell'\kappa') \ . \qquad (2.64)$$

This follows from Eqs. (1.54) and (1.56) and the coefficients $\phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa')$ are defined by Eq. (1.57c). By performing an isotropic, homogeneous deformation Eq. (2.18), one can show that the perturbations to the force constants $\phi_{\alpha\beta}(\ell\kappa|\ell'\kappa')$ defined by Eq. (1.57b) are

$$\phi^{(1)}_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \sum_\gamma \phi_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa') R_\gamma(\ell\kappa|\ell'\kappa'). \quad (2.65)$$

FIRST NEIGHBOR CONTRIBUTION

By direct computation using Eq. (2.65), we have in complete analogy with Eq. (1.68) that

$$\overset{\leftrightarrow}{\phi}{}^{(1)}(0,0|\delta_1,1) = \begin{pmatrix} \alpha^{(1)} & \beta^{(1)} & \beta^{(1)} \\ \beta^{(1)} & \alpha^{(1)} & \beta^{(1)} \\ \beta^{(1)} & \beta^{(1)} & \alpha^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\delta_2,1) = \begin{pmatrix} \alpha^{(1)} & \beta^{(1)} & -\beta^{(1)} \\ \beta^{(1)} & \alpha^{(1)} & -\beta^{(1)} \\ -\beta^{(1)} & -\beta^{(1)} & \alpha^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\delta_3,1) = \begin{pmatrix} \alpha^{(1)} & -\beta^{(1)} & -\beta^{(1)} \\ -\beta^{(1)} & \alpha^{(1)} & \beta^{(1)} \\ -\beta^{(1)} & \beta^{(1)} & \alpha^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\delta_4,1) = \begin{pmatrix} \alpha^{(1)} & -\beta^{(1)} & \beta^{(1)} \\ -\beta^{(1)} & \alpha^{(1)} & -\beta^{(1)} \\ \beta^{(1)} & -\beta^{(1)} & \alpha^{(1)} \end{pmatrix} \qquad (2.66)$$

where we have defined

$$\alpha^{(1)} = \left[\frac{r_o}{3}\phi_1'''(r_o) + \frac{2}{3}\phi_1''(r_o) - \frac{2}{3}\frac{\phi_1'(r_o)}{r_o}\right] \qquad (2.67a)$$

$$\beta^{(1)} = \left[\frac{r_o}{3}\phi_1'''(r_o) - \frac{1}{3}\phi_1''(r_o) + \frac{1}{3r_o}\phi_1'(r_o)\right] . \qquad (2.67b)$$

Note also that

$$(\alpha^{(1)} - \beta^{(1)}) = \left[\phi_1''(r_o) - \frac{\phi_1'(r_o)}{r_o}\right] . \qquad (2.68)$$

Using Eq. (2.41) and the analogy with Eq. (1.25) we can write down the first neighbor, central potential perturbation to the dynamical matrix

$$D^{(1)1^{o}}_{\alpha\beta}(0,1|\vec{k}) = -\frac{1}{M}\sum_{i=1}^{4}\phi^{(1)}_{\alpha\beta}(0,0|\delta_i,1)e^{i\vec{k}\cdot\vec{\delta}_i} ,\tag{2.69a}$$

and

$$\overset{=}{D}^{(1)1^{o}}(0,0|\vec{k}) = \frac{4\alpha^{(1)}}{M}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} .\tag{2.69b}$$

The $\vec{\delta}_i$ are defined by Eq. (1.62).

SECOND NEIGHBOR CONTRIBUTION

The matrices analogous to Eq. (1.80) are

$$\overleftrightarrow{\Phi}^{(1)}(0,0|\mu_1,0) = \begin{pmatrix} \mu^{(1)} & \nu^{(1)} & 0 \\ \nu^{(1)} & \mu^{(1)} & 0 \\ 0 & 0 & \lambda^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\Phi}^{(1)}(0,0|\mu_2,0) = \begin{pmatrix} \lambda^{(1)} & 0 & 0 \\ 0 & \mu^{(1)} & \nu^{(1)} \\ 0 & \nu^{(1)} & \mu^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\Phi}^{(1)}(0,0|\mu_3,0) = \begin{pmatrix} \mu^{(1)} & 0 & \nu^{(1)} \\ 0 & \lambda^{(1)} & 0 \\ \nu^{(1)} & 0 & \mu^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\Phi}^{(1)}(0,0|\mu_4,0) = \begin{pmatrix} \mu^{(1)} & -\nu^{(1)} & 0 \\ -\nu^{(1)} & \mu^{(1)} & 0 \\ 0 & 0 & \lambda^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\Phi}^{(1)}(0,0|\mu_5,0) = \begin{pmatrix} \lambda^{(1)} & 0 & 0 \\ 0 & \mu^{(1)} & -\nu^{(1)} \\ 0 & -\nu^{(1)} & \mu^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\Phi}^{(1)}(0,0|\mu_6,0) = \begin{pmatrix} \mu^{(1)} & 0 & -\nu^{(1)} \\ 0 & \lambda^{(1)} & 0 \\ -\nu^{(1)} & 0 & \mu^{(1)} \end{pmatrix} . \tag{2.70}$$

Here we have defined

$$\mu^{(1)} = \frac{1}{2}(r_2\phi_2'''(r_2) + \phi_2''(r_2) - \phi_2'(r_2)/r_2) \qquad (2.71a)$$

$$\nu^{(1)} = \frac{1}{2}(r_2\phi_2'''(r_2) - \phi_2''(r_2) + \phi_2'(r_2)/r_2) \qquad (2.71b)$$

$$\lambda^{(1)} = (\mu^{(1)} - \nu^{(1)}) = (\phi_2''(r_2) - \phi_2'(r_2)/r_2) \ . \qquad (2.71c)$$

Thus we find that

$$D_{\alpha\beta}^{(1)2^{o}}(0,1|\vec{k}) = 0 \qquad (2.72a)$$

and

$$D_{\alpha\beta}^{(1)2^{o}}(0,0|\vec{k}) = \frac{2}{M}\sum_{i=1}^{6} \phi_{\alpha\beta}^{(1)}(0,0|\mu_i,0)[1 - \cos(\vec{k}\cdot\vec{\mu}_i)] \ . \qquad (2.72b)$$

The $\vec{\mu}_i$ are defined by Eq. (1.75).

THIRD NEIGHBOR CONTRIBUTION

The matrices analogous to Eq. (1.88) are

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_1,1) = \begin{pmatrix} \mu'^{(1)} & -\nu'^{(1)} & \delta'^{(1)} \\ -\nu'^{(1)} & \mu'^{(1)} & -\delta'^{(1)} \\ \delta'^{(1)} & -\delta'^{(1)} & \lambda'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_2,1) = \begin{pmatrix} \mu'^{(1)} & -\delta'^{(1)} & \nu'^{(1)} \\ -\delta'^{(1)} & \lambda'^{(1)} & -\delta'^{(1)} \\ \nu'^{(1)} & -\delta'^{(1)} & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_3,1) = \begin{pmatrix} \lambda'^{(1)} & -\delta'^{(1)} & \delta'^{(1)} \\ -\delta'^{(1)} & \mu'^{(1)} & -\nu'^{(1)} \\ \delta'^{(1)} & -\nu'^{(1)} & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_4,1) = \begin{pmatrix} \mu'^{(1)} & -\nu'^{(1)} & -\delta'^{(1)} \\ -\nu'^{(1)} & \mu'^{(1)} & \delta'^{(1)} \\ -\delta'^{(1)} & \delta'^{(1)} & \lambda'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_5,1) = \begin{pmatrix} \mu'^{(1)} & -\delta'^{(1)} & -\nu'^{(1)} \\ -\delta'^{(1)} & \lambda'^{(1)} & \delta'^{(1)} \\ -\nu'^{(1)} & \delta'^{(1)} & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_6,1) = \begin{pmatrix} \lambda'^{(1)} & -\delta'^{(1)} & -\delta'^{(1)} \\ -\delta'^{(1)} & \mu'^{(1)} & \nu'^{(1)} \\ -\delta'^{(1)} & \nu'^{(1)} & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_7,1) = \begin{pmatrix} \mu'^{(1)} & \nu'^{(1)} & -\delta'^{(1)} \\ \nu'^{(1)} & \mu'^{(1)} & -\delta'^{(1)} \\ -\delta'^{(1)} & -\delta'^{(1)} & \lambda'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_8,1) = \begin{pmatrix} \lambda'^{(1)} & \delta'^{(1)} & -\delta'^{(1)} \\ \delta'^{(1)} & -\mu'^{(1)} & \nu'^{(1)} \\ -\delta'^{(1)} & -\nu'^{(1)} & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_9,1) = \begin{pmatrix} \mu'^{(1)} & \delta'^{(1)} & -\nu'^{(1)} \\ \delta'^{(1)} & \lambda'^{(1)} & -\delta'^{(1)} \\ -\nu'^{(1)} & -\delta'^{(1)} & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_{10},1) = \begin{pmatrix} \mu'^{(1)} & \nu'^{(1)} & \delta'^{(1)} \\ \nu'^{(1)} & \mu'^{(1)} & \delta'^{(1)} \\ \delta'^{(1)} & \delta'^{(1)} & \lambda'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_{11},1) = \begin{pmatrix} \lambda'^{(1)} & \delta'^{(1)} & \delta'^{(1)} \\ \delta'^{(1)} & \mu'^{(1)} & \nu'^{(1)} \\ \delta'^{(1)} & \nu'^{(1)} & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\tau_{12},1) = \begin{pmatrix} \mu'^{(1)} & \delta'^{(1)} & \nu'^{(1)} \\ \delta'^{(1)} & \lambda'^{(1)} & \delta'^{(1)} \\ \nu'^{(1)} & \delta'^{(1)} & \mu'^{(1)} \end{pmatrix}. \qquad (2.73)$$

Here we have defined

$$\mu'^{(1)} = \frac{1}{11}[r_3\phi_3'''(r_3)+10\phi_3''(r_3)-10\phi_3'(r_3)/r_3] \qquad (2.74a)$$

$$\nu'^{(1)} = \frac{1}{11}[r_3\phi_3'''(r_3)-\phi_3''(r_3)+\phi_3'(r_3)/r_3] \qquad (2.74b)$$

$$\delta'^{(1)} = 3\nu'^{(1)} = \frac{3}{11}[r_3\phi_3'''(r_3)-\phi_3''(r_3)+\phi_3'(r_3)/r_3]$$

$$(2.74c)$$

$$\lambda'^{(1)} = (\mu'^{(1)}+8\nu'^{(1)}) =$$

$$= \left[\frac{9}{11}r_3\phi_3'''(r_3) + \frac{2}{11}\,\phi_3''(r_3) - \frac{2}{11}\,\frac{\phi_3'(r_3)}{r_3}\right] \qquad (2.74d)$$

Thus we find that

$$D^{(1)3^o}_{\alpha\beta}(0,1|\vec{k}) = -\frac{1}{M}\sum_{i=1}^{12}\phi^{(1)}_{\alpha\beta}(0,0,|\tau_i,1)e^{i\vec{k}\cdot\vec{\tau}_i}$$

$$(2.75a)$$

and

$$\overleftrightarrow{D}^{(1)3^o}(0,0|\vec{k}) = \frac{(8\mu'^{(1)}+4\lambda'^{(1)})}{M}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}. \qquad (2.76b)$$

The $\vec{\tau}_i$ are defined by Eq. (1.85).

FOURTH NEIGHBOR CONTRIBUTION

The matrices analogous to Eq. (1.97) are

$$\overleftrightarrow{\phi}^{(1)}(0,0|\lambda_1,0) = \begin{pmatrix} \lambda'^{(1)} & 0 & 0 \\ 0 & \mu'^{(1)} & 0 \\ 0 & 0 & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\lambda_2,0) = \begin{pmatrix} \mu'^{(1)} & 0 & 0 \\ 0 & \lambda'^{(1)} & 0 \\ 0 & 0 & \mu'^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{\phi}^{(1)}(0,0|\lambda_3,0) = \begin{pmatrix} \mu'^{(1)} & 0 & 0 \\ 0 & \mu'^{(1)} & 0 \\ 0 & 0 & \lambda'^{(1)} \end{pmatrix} . \qquad (2.76)$$

Here we have defined

$$\lambda'^{(1)} = a\phi_4'''(a) \qquad (2.77a)$$

$$\mu'^{(1)} = [\phi_4''(a) - \frac{1}{a}\phi_4'(a)] \ . \qquad (2.77b)$$

Thus we find that

$$D_{\alpha\beta}^{(1)4^o}(0,1|\vec{k}) = 0 \ , \qquad (2.78)$$

and

$$D^{(1)4^\circ}_{\alpha\beta}(0,0|\vec{k}) = D^{(1)4^\circ}_{\alpha\alpha}(0,0|\vec{k})\delta_{\alpha\beta} \ , \qquad (2.79)$$

with

$$D^{(1)4^\circ}_{11}(0,0|\vec{k}) = \frac{4}{M}\left[\lambda''^{(1)}\sin^2\left(\frac{k_1 a}{2}\right)+\mu''^{(1)}\sin^2\left(\frac{k_2 a}{2}\right)+ + \mu''^{(1)}\sin^2\left(\frac{k_3 a}{2}\right)\right] \qquad (2.80a)$$

$$D^{(1)4^\circ}_{22}(0,0|\vec{k}) = \frac{4}{M}\left[\mu''^{(1)}\sin^2\left(\frac{k_1 a}{2}\right)+\lambda''^{(1)}\sin^2\left(\frac{k_2 a}{2}\right)+ + \mu''^{(1)}\sin^2\left(\frac{k_3 a}{2}\right)\right] \qquad (2.80b)$$

$$D^{(1)4^\circ}_{33}(0,0|\vec{k}) = \frac{4}{M}\left[\mu''^{(1)}\sin^2\left(\frac{k_1 a}{2}\right)+\mu''^{(1)}\sin^2\left(\frac{k_2 a}{2}\right)+ + \lambda''^{(1)}\sin^2\left(\frac{k_3 a}{2}\right)\right] . \qquad (2.80c)$$

Here k_1, k_2, k_3 are the cartesian components of the wavevector defined by Eq. (1.101).

ANGLE BENDING CONTRIBUTION

As was mentioned in Chapter 1, the angle bending potential energy Eq. (1.104) contains anharmonic terms when expressed in terms of the displacements $\vec{u}(\ell\kappa)$. In order to calculate the perturbation to the dynamical matrix, Eq. (2.41), caused by the angle bending anharmonicity, it is only necessary to obtain the dynamical matrix with the deformation Eq. (2.18) present, and then separate out the term linear in ϵ . This approach is chosen since the angle bending contribution to the dynamical matrix has already been obtained in the strict harmonic approximation.

Using Eqs. (1.114) and (2.18) we have

$$\vec{x}(\ell\kappa|\ell'\kappa') = (1+\epsilon)\vec{R}(\ell\kappa|\ell'\kappa') + \vec{v}(\ell\kappa|\ell'\kappa') \ . \quad (2.81)$$

Since the deformation is isotropic, it is clear from Eqs. (1.113) and (1.115) that the angles when all the $\vec{v}(\ell\kappa)$ are zero are the same as the equilibrium angles. By using Eq. (2.81) and carrying out an expansion similar to the one leading to Eq. (1.117), we obtain the change in angle correct to first order in the displacements $\vec{v}(\ell\kappa)$ and all orders in ϵ

$$\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \frac{1}{(1+\epsilon)}\sum_{\alpha}\eta_{\alpha}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')v_{\alpha}(\ell\kappa|\ell'\kappa')$$

$$+ \frac{1}{(1+\epsilon)}\sum_{\alpha}\eta_{\alpha}(\ell\kappa|\ell''\kappa''|\ell'\kappa')v_{\alpha}(\ell\kappa|\ell''\kappa'') \ . \quad (2.82)$$

Here the $\eta_\alpha(\ell\kappa|\ell'\kappa'|\ell''\kappa'')$ are defined by Eq. (1.118) in terms of the undeformed or "bare" position vectors $\vec{R}(\ell\kappa)$.

Equation (2.82) differs from Eq. (1.117) by the factor $(1+\epsilon)^{-1}$ and the fact that we are using the displacements $\vec{v}(\ell\kappa)$. Since we square the angle changes in Eq. (1.104), the only difference between the angle bending potential energy which is quadratic in the displacements $\vec{u}(\ell\kappa)$ and that which is quadratic in the displacements $\vec{v}(\ell\kappa)$ is that a factor of $(1+\epsilon)^{-2}$ appears in front of the latter. Thus the angle bending contribution to the dynamical matrix with the strain present is the same as without the strain, Eqs. (1.124) and (1.125), but with the force constant σ replaced by $\tilde{\sigma}$ where

$$\tilde{\sigma} = \frac{\sigma}{(1+\epsilon)^2} . \tag{2.83}$$

The contribution to first order in ϵ is

$$\tilde{\sigma} = \sigma + \epsilon\sigma^{(1)} + \cdots , \tag{2.84}$$

where from Eq. (2.83) we have

$$\sigma^{(1)} = - 2\sigma . \tag{2.85}$$

Thus the angle bending perturbation to the dynamical matrix $D^{(1)(\theta)}_{\alpha\beta}(\kappa\kappa'|\vec{k})$ is given by Eqs. (1.124) and (1.125) with σ replaced by $\sigma^{(1)}$ everywhere. Rather than reproduce the lengthy expressions which are obtained trivially from Eqs. (1.124) and (1.125), we give an example for one element

$$D_{12}^{(1)(\theta)}(0,1|\vec{k}) = \frac{4\sigma^{(1)}}{3M}\left(1+e^{i\vec{k}\cdot\vec{\delta}_2}-e^{i\vec{k}\cdot\vec{\delta}_2}-e^{i\vec{k}\cdot\vec{\delta}_3}-e^{i\vec{k}\cdot\vec{\delta}_4}\right) . \tag{2.86}$$

Eq. (2.86) is the analog of Eq. (1.125b). The $\vec{\delta}_i$ are given by Eq. (1.62a).

The result Eq. (2.85) is rather interesting because it predicts that the angle bending force constant perturbation is given in terms of the parameter σ that is determined by the harmonic model. Thus this type of anharmonicity requires no additional parameters that cannot be determined from the harmonic model. This is in contrast to the central potential anharmonicity which requires the third derivatives of the potential as additional parameters that are not determined by the harmonic model. To our knowledge, the result Eq. (2.85) has not been obtained previously.

NONLOCAL DIPOLE CONTRIBUTION

In order to compute the dipole contribution to the anharmonicity, we must generalize Eq. (1.129) to include terms quadratic in the displacements so that

$$p_\alpha(\ell\kappa) = \sum_{\ell'\kappa'\beta} p_{\alpha\beta}(\ell\kappa|\ell'\kappa')u_\beta(\ell'\kappa') + \frac{1}{2}\sum_{\substack{\ell'\kappa'\beta\\ \ell''\kappa''\gamma}} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')u_\beta(\ell'\kappa')u_\gamma(\ell''\kappa'') \ . \tag{2.87}$$

Here we have defined

$$p_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \left.\frac{\partial p_\alpha(\ell\kappa)}{\partial u_\beta(\ell'\kappa')}\right|_o \ , \tag{2.88a}$$

and

$$p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \left.\frac{\partial^2 p_\alpha(\ell\kappa)}{\partial u_\beta(\ell'\kappa')\partial u_\gamma(\ell''\kappa'')}\right|_o \ . \tag{2.88b}$$

The total dipole moment of the crystal Eq. (1.130) can then be written as

$$P_\alpha = \frac{1}{2}\sum_{\ell\kappa}\sum_{\ell'\kappa'\beta}\sum_{\ell''\kappa''\gamma} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')u_\beta(\ell'\kappa')u_\gamma(\ell''\kappa'') \ , \tag{2.89}$$

where we have taken account of the fact that the term linear in the displacements was shown to vanish in Chapter

1 (Eq. (1.140)). Defining

$$M_{\alpha\beta\gamma}(\ell'\kappa'|\ell''\kappa'') = \sum_{\ell\kappa} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') \ , \qquad (2.90)$$

we have

$$p_\alpha = \frac{1}{2} \sum_{\ell\kappa\beta} \sum_{\ell'\kappa'\gamma} M_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa')u_\beta(\ell\kappa)u_\gamma(\ell'\kappa') \ . \qquad (2.91)$$

Eq. (2.91) leads to the two-phonon infra-red spectrum of diamond structure crystals.[18]

If we substitute Eq. (2.87) into the dipole-dipole interaction energy, Eqs. (1.153) and (1.155), the resulting expression will contain cubic and quartic anharmonic terms in addition to the harmonic term treated in Chapter 1. The perturbation to the dynamical matrix can be determined by computing the dynamical matrix with the strain present and then separating out the term linear in ϵ .

Substituting Eq. (2.18) into Eq. (2.87) we obtain

$$\begin{aligned} p_\alpha(\ell\kappa) = {} & \epsilon p_\alpha^{(1)}(\ell\kappa) + \epsilon^2 p_\alpha^{(2)}(\ell\kappa) + \\ & + \sum_{\ell'\kappa'\beta} p_{\alpha\beta}(\ell\kappa|\ell'\kappa')v_\beta(\ell'\kappa\ell) + \\ & + \epsilon \sum_{\ell'\kappa'\beta} p_{\alpha\beta}^{(1)}(\ell\kappa|\ell'\kappa')v_\beta(\ell'\kappa') + \\ & + \frac{1}{2} \sum_{\substack{\ell'\kappa'\beta \\ \ell''\kappa''\gamma}} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')v_\beta(\ell'\kappa')v_\gamma(\ell''\kappa'') \ , \end{aligned} \qquad (2.92)$$

where we have defined

$$p_{\alpha}^{(1)}(\ell\kappa) = \sum_{\ell'\kappa'\beta} p_{\alpha\beta}(\ell\kappa|\ell'\kappa')R_{\beta}(\ell'\kappa') \ , \tag{2.93a}$$

$$p_{\alpha}^{(2)}(\ell\kappa) = \frac{1}{2} \sum_{\substack{\ell'\kappa'\beta \\ \ell''\kappa''\gamma}} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_{\beta}(\ell'\kappa')R_{\gamma}(\ell''\kappa'') \ , \tag{2.93b}$$

and

$$p_{\alpha\beta}^{(1)}(\ell\kappa|\ell'\kappa') = \sum_{\ell''\kappa''\gamma} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')R_{\gamma}(\ell''\kappa'') . \tag{2.93c}$$

At this point we impose infinitesimal translation invariance on the moments $p_{\alpha}(\ell\kappa)$. Note that the results of Chapter 1, Eqs. (1.149), satisfy infinitesimal translation invariance without ever imposing this condition on the moments $p_{\alpha}(\ell\kappa)$. Imposing this requirement on Eq. (2.87) we obtain the conditions

$$\sum_{\ell'\kappa'} p_{\alpha\beta}(\ell .|\ell'\kappa') = 0 \ , \tag{2.94a}$$

and

$$\sum_{\ell''\kappa''} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \sum_{\ell'\kappa'} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = 0 \ . \tag{2.94b}$$

Infinitesimal translation invariance of the total dipole moment Eq. (1.130) only yields the less restrictive conditions that

$$\sum_{\ell\kappa} \sum_{\ell'\kappa'} p_{\alpha\beta}(\ell\kappa|\ell'\kappa') = 0 \;, \tag{2.95a}$$

and

$$\sum_{\ell\kappa} \sum_{\ell'\kappa'} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \sum_{\ell\kappa} \sum_{\ell''\kappa''} p_{\alpha\beta\gamma}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = 0 \;. \tag{2.95b}$$

Using Eqs. (2.94), (1.142) and the transformation property under the space group operation $\{S|\vec{v}(S)+\vec{R}(m)\}$ that

$$p_{\alpha\beta\gamma}(LK|L'K'|L''K'') = \sum_{\mu\nu\lambda} S_{\alpha\mu}S_{\beta\nu}S_{\gamma\lambda}\,p_{\mu\nu\lambda}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') \;, \tag{2.96}$$

it is easy to show that $p_{\alpha}^{(1)}(\ell\kappa)$ and $p_{\alpha}^{(2)}(\ell\kappa)$ transform in the same manner as the first order atomic force constants. Thus by the same arguments as presented in Appendix F, $p_{\alpha}^{(1)}(\ell\kappa)$ and $p_{\alpha}^{(2)}(\ell\kappa)$ are both zero in the diamond structure. Similarly, one can show using Eqs. (2.94b) and (2.96) that the coefficients $p_{\alpha\beta}^{(1)}(\ell\kappa|\ell'\kappa')$ have the same symmetry properties as the $p_{\alpha\beta}(\ell\kappa|\ell'\kappa')$. Thus we can use Eq. (1.150) to write

$$\overleftrightarrow{p}^{(1)}(0,0|\delta_1,1) = \begin{pmatrix} p_1^{(1)} & p_2^{(1)} & p_2^{(1)} \\ p_2^{(1)} & p_1^{(1)} & p_2^{(1)} \\ p_2^{(1)} & p_2^{(1)} & p_1^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{p}^{(1)}(0,0|\delta_2,1) = \begin{pmatrix} p_1^{(1)} & p_2^{(1)} & -p_2^{(1)} \\ p_2^{(1)} & p_1^{(1)} & -p_2^{(1)} \\ -p_2^{(1)} & -p_2^{(1)} & p_1^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{p}^{(1)}(0,0|\delta_3,1) = \begin{pmatrix} p_1^{(1)} & -p_2^{(1)} & -p_2^{(1)} \\ -p_2^{(1)} & p_1^{(1)} & p_2^{(1)} \\ -p_2^{(1)} & p_2^{(1)} & p_1^{(1)} \end{pmatrix}$$

$$\overleftrightarrow{p}^{(1)}(0,0|\delta_4,1) = \begin{pmatrix} p_1^{(1)} & -p_2^{(1)} & p_2^{(1)} \\ -p_2^{(1)} & p_1^{(1)} & -p_2^{(1)} \\ p_2^{(1)} & -p_2^{(1)} & p_1^{(1)} \end{pmatrix} . \tag{2.97}$$

We also have for the case of nearest neighbor nonlocality that

$$p_{\alpha\beta}^{(1)}(0,0|0,0) = -4p_1^{(1)}\delta_{\alpha\beta} . \tag{2.98}$$

Here $p_1^{(1)}$ and $p_2^{(1)}$ are parameters to be determined and have the units of charge. From the preceding remarks and Eqs. (2.92), (2.97), (2.98) and (1.49) we can write

$$p_\alpha(\ell,0) = \sum_\beta \sum_{i=1}^{4} \tilde{p}_{\alpha\beta}(0,0|\delta_i,1)(v_\beta(\ell+\delta_i,1)-v_\beta(\ell,0)) + \frac{1}{2}\sum_{\substack{\ell'\kappa'\beta \\ \ell''\kappa''\gamma}} p_{\alpha\beta\gamma}(\ell,0|\ell'\kappa'|\ell''\kappa'')v_\beta(\ell'\kappa')v_\gamma(\ell''\kappa'') , \tag{2.99a}$$

$$p_\alpha(\ell,1) = \sum_\beta \sum_{i=1}^{4} \tilde{p}_{\alpha\beta}(0,0|\delta_i,1)(v_\beta(\ell-\delta_i,0)-v_\beta(\ell,1)) + \frac{1}{2}\sum_{\substack{\ell'\kappa'\beta \\ \ell''\kappa''\gamma}} p_{\alpha\beta\gamma}(\ell,1|\ell'\kappa'|\ell''\kappa'')v_\beta(\ell'\kappa')v_\gamma(\ell''\kappa'') , \tag{2.99b}$$

where we have defined

$$\tilde{p}_{\alpha\beta}(\ell\kappa|\ell'\kappa') = p_{\alpha\beta}(\ell\kappa|\ell'\kappa') + \epsilon\; p_{\alpha\beta}^{(1)}(\ell\kappa|\ell'\kappa') . \tag{2.100}$$

In order to compute the dipole contribution to the dynamical matrix with the deformation present, it is only necessary to keep the terms linear in the displacements $v_\alpha(\ell\kappa)$ in Eqs. (2.99). This is so since the quadratic terms give rise to terms in the potential energy that are cubic and quartic in the $v_\alpha(\ell\kappa)$. Thus we see that it is only necessary to replace p_1 and p_2 in Eqs. (1.165) by their renormalized counterparts $\tilde{p}_1$ and $\tilde{p}_2$ where

$$\tilde{p}_1 = p_1 + \epsilon p_1^{(1)} , \tag{2.101a}$$

$$\tilde{p}_2 = p_2 + \epsilon p_2^{(1)} . \tag{2.101b}$$

Separating off the terms linear in ϵ we obtain the perturbation to the dipole contribution to the dynamical matrix

$$D_{\alpha\beta}^{(1)dd}(0,0|\vec{k}) = \frac{8\pi p_1 p_1^{(1)}}{\epsilon_s M\Omega_o} T_{\alpha\beta}^{11}(\vec{k}) + \\ + \frac{4\pi(p_1 p_2^{(1)} + p_2 p_1^{(1)})}{\epsilon_s M\Omega_o} T_{\alpha\beta}^{12}(\vec{k}) \\ + \frac{8\pi p_2 p_2^{(1)}}{\epsilon_s M\Omega_o} T_{\alpha\beta}^{22}(\vec{k}) \;, \tag{2.102a}$$

$$D_{\alpha\beta}^{(1)dd}(0,1|\vec{k}) = \frac{8\pi p_1 p_1^{(1)}}{\epsilon_s M\Omega_o} V_{\alpha\beta}^{11}(\vec{k}) + \\ + \frac{4\pi(p_1 p_2^{(1)} + p_2 p_1^{(1)})}{\epsilon_s M\Omega_o} V_{\alpha\beta}^{12}(\vec{k}) \\ + \frac{8\pi p_2 p_2^{(1)}}{\epsilon_s M\Omega_o} V_{\alpha\beta}^{22}(\vec{k}) \;. \tag{2.102b}$$

The matrices $T_{\alpha\beta}^{11}(\vec{k})$, $T_{\alpha\beta}^{12}(\vec{k})$, $T_{\alpha\beta}^{22}(\vec{k})$, $V_{\alpha\beta}^{11}(\vec{k})$, $V_{\alpha\beta}^{12}(\vec{k})$ and $V_{\alpha\beta}^{22}(\vec{k})$ are defined by Eqs. (1.166) and (1.167). In Eqs. (2.102) ϵ_s is the static dielectric constant, not to be confused with the strain parameter ϵ . Note the interesting way in which the harmonic and anharmonic parameters both play a role in Eqs. (2.102).

GRÜNEISEN PARAMETERS

In order to compute the Grüneisen parameters, there are two alternative but equivalent methods. One method is to simply use Eqs. (2.43) and (2.51) and directly compute. This method is well suited for numerical work at an arbitrary $\vec{k}$ point once we have obtained the eigenvectors. The other method is to compute the quasiharmonic frequency $\tilde{\omega}(\vec{k}j)$ defined by the eigenvalue equation

$$\tilde{\omega}^2(\vec{k}j)\tilde{e}_\alpha(\kappa|\vec{k}j) = \sum_{\kappa'\beta}\tilde{D}_{\alpha\beta}(\kappa\kappa'|\vec{k})\tilde{e}_\beta(\kappa'|\vec{k}j) , \quad (2.103)$$

with

$$\tilde{D}_{\alpha\beta}(\kappa\kappa'|\vec{k}) = D_{\alpha\beta}(\kappa\kappa'|\vec{k}) + \epsilon D^{(1)}_{\alpha\beta}(\kappa\kappa'|\vec{k}) . \quad (2.104)$$

It is easy to show using first-order perturbation theory that

$$\left.\frac{\partial\tilde{\omega}^2(\vec{k}j)}{\partial\epsilon}\right|_{\epsilon=0} = \omega_1^2(\vec{k}j) = \sum_{\substack{\kappa\alpha \\ \kappa'\beta}} e^*_\alpha(\kappa|\vec{k}j)D^{(1)}_{\alpha\beta}(\kappa\kappa'|\vec{k})e_\beta(\kappa'|\vec{k}j) . \quad (2.105)$$

Using Eq. (2.51) we can write

$$\gamma(\vec{k}j) = -\frac{1}{6\omega^2(\vec{k}j)}\left[\frac{\partial\tilde{\omega}^2(\vec{k}j)}{\partial\epsilon}\right]_{\epsilon=0} . \quad (2.106)$$

Thus we see that if we have an analytic expression for the quasiharmonic frequency of a given mode, one can differentiate analytically and use Eq. (2.106) to obtain the mode gamma.

The quasiharmonic expressions for the frequencies can be easily obtained from the harmonic ones by simply replacing the harmonic model force constants by the quasiharmonic force constants according to the prescription

$$\tilde{\Phi}_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') + \epsilon\Phi^{(1)}_{\alpha\beta}(\ell\kappa|\ell'\kappa') \ . \tag{2.107}$$

Since we have already obtained expressions for the harmonic frequencies of several modes in Chapter 1, we will adopt this second method to obtain analytic expressions for the mode gammas. Note that both methods give identical results but are different computational schemes.

[100] DIRECTION

In this section we list some results that can be easily obtained from Chapter 1. As an example, consider first the Raman mode. Using Eq. (1.190) we can write

$$\tilde{\omega}_{RA}^{2} = \frac{1}{M}\left(8\tilde{\alpha} + \frac{64}{3}\,\tilde{\sigma} + 16\tilde{\mu}' + 8\tilde{\lambda}'\right) , \qquad (2.108)$$

where

$$\tilde{\alpha} = \alpha + \epsilon\alpha^{(1)} , \qquad (2.109a)$$

$$\tilde{\alpha}' = \mu' + \epsilon\mu'^{(1)} , \qquad (2.109b)$$

$$\tilde{\lambda}' = \lambda' + \epsilon\lambda'^{(1)} . \qquad (2.109c)$$

Thus

$$\frac{\partial\tilde{\omega}_{RA}^{2}}{\partial\epsilon} = \frac{1}{M}\left(8\alpha^{(1)} + \frac{64}{3}\,\sigma^{(1)} + 16\mu'^{(1)} + 8\lambda'^{(1)}\right) , \qquad (2.110)$$

and using Eq. (2.106) we obtain

$$\gamma_{RA} \simeq - \frac{1}{6M\omega_{RA}^{2}}\left(8\alpha^{(1)} + \frac{64}{3}\,\sigma^{(1)} + 16\mu'^{(1)} + 8\lambda'^{(1)}\right) . \qquad (2.111)$$

This can be written in terms of the potential derivatives as

$$\gamma_{RA} = -\frac{1}{3M\omega_{RA}^2}\left(\frac{4r_o}{3}\,\phi_1'''(r_o) + \frac{8}{3}\,\phi_1'(r_o) - \frac{8}{3}\,\frac{\phi_1'(r_o)}{r_o}\right.$$

$$\left. + 4r_3\phi_3'''(r_3) + 8\phi_3''(r_3) - \frac{8\phi_3'(r_3)}{r_3} - \frac{64}{3}\,\sigma\right) \quad , \tag{2.112}$$

where we have used Eqs. (2.67a), (2.74) and (2.85).

At the zone boundary we obtain from Eq. (1.192)

$$\gamma_{LOX} = \gamma_{LAX} = -\frac{1}{3M\omega_{LAX}^2}\left[2\alpha^{(1)} + \frac{20}{3}\sigma^{(1)} + 8\mu^{(1)} + 4\mu'^{(1)} + 2\lambda'^{(1)}\right.$$

$$\left. + \frac{4\pi p_1 p_1^{(1)}}{\epsilon_s \Omega_o}\,T_{11}^{11}(X)\right], \tag{2.113}$$

or

$$\gamma_{LAX} = -\frac{2}{3M\omega_{LAX}^2}\left[\frac{r_o}{3}\,\phi_1'''(r_o) + \frac{2}{3}\,\phi_1''(r_o) - \frac{2}{3}\,\frac{\phi_1'(r_o)}{r_o}\right.$$

$$+ 2r_2\phi_2'''(r_2) + 2\phi_2''(r_2) - \frac{2\phi_2'(r_2)}{r_2}$$

$$+ r_3\phi_3'''(r_3) + 2\phi_3''(r_3) - \frac{2\phi_3'(r_3)}{r_3}$$

$$\left. - \frac{20}{3}\,\sigma + \frac{2\pi p_1 p_1^{(1)}}{\epsilon_s \Omega_o}\,T_{11}^{11}(X)\right] \quad . \tag{2.114}$$

From Eq. (1.200) we obtain

$$\gamma_{TAX} = -\frac{1}{3M\omega_{TAX}^2}\left[2\alpha^{(1)}-2\beta^{(1)}+4\mu^{(1)}+4\lambda^{(1)}+4\mu'^{(1)}+2\lambda'^{(1)} - 2\nu'^{(1)}+4\delta'^{(1)}+6\sigma^{(1)} + \frac{4\pi}{\epsilon_s\Omega_o}(p_1-p_2)(p_1^{(1)}-p_2^{(1)})(T^{11}_{22}(X)+V^{11}_{23}(X))\right], \quad (2.115)$$

or in terms of potential derivatives

$$\gamma_{TAX} = -\frac{2}{3M\omega_{TAX}^2}\left[\phi_1''(r_o) - \frac{\phi_1'(r_o)}{r_o} + r_2\phi_2'''(r_2) + 3\phi_2''(r_2) - \frac{3\phi_2'(r_2)}{r_2} + \frac{16}{11}r_3\phi_3'''(r_3) + \frac{17}{11}\phi_3''(r_3) - \frac{17}{11}\frac{\phi_3'(r_3)}{r_3} - 6\sigma + \frac{2\pi}{\epsilon_s\Omega_o}(p_1-p_2)(p_1^{(1)}-p_2^{(1)})(T^{11}_{22}(X)+V^{11}_{23}(X))\right], \quad (2.116)$$

where from Eq. (1.202) we have

$$T^{11}_{22}(X) + V^{11}_{23}(X) = -16.28143 \ . \quad (2.117)$$

Similarly from Eq. (1.201) we obtain

$$\gamma_{TOX} = -\frac{1}{3M\omega_{TOX}^2}\left[2\alpha^{(1)}+2\beta^{(1)}+4\mu^{(1)}+4\lambda^{(1)}+4\mu'^{(1)}+2\lambda'^{(1)} + 2\nu'^{(1)} - 4\delta'^{(1)} + \frac{2}{3}\sigma^{(1)} + \frac{4\pi}{\epsilon_s\Omega_o}(p_1+p_2)(p_1^{(1)}+p_2^{(1)})(T^{11}_{22}(X)-V^{11}_{23}(X))\right]. \quad (2.118)$$

In terms of the potential derivatives

$$\gamma_{TOX} = -\frac{2}{3M\omega_{TOX}^{2}}\left[\frac{2}{3}\, r_o\phi_1'''(r_o) + \frac{1}{3}\,\phi_1''(r_o) - \frac{1}{3}\,\frac{\phi_1'(r_o)}{r_o} + r_2\phi_2'''(r_2) + 3\phi_2''(r_2) - \frac{3\phi_2'(r_2)}{r_2} + \frac{6}{11}\, r_3\phi_3'''(r_3) + \frac{27}{11}\,\phi_3''(r_3) - \frac{27\phi_3'(r_3)}{11r_3} - \frac{2\sigma}{3} + \frac{2\pi}{\epsilon_s\Omega_o}(p_1+p_2)(p_1^{(1)}+p_2^{(1)})(T_{22}^{11}(X) - V_{23}^{11}(X))\right], \tag{2.119}$$

where from Eq. (1.202) we have

$$T_{22}^{11}(X) - V_{23}^{11}(X) = 10.76338\ . \tag{2.120}$$

In the elastic region we have

$$\gamma_{LA[100]}^{(el)} = -\frac{1}{6C_{11}}\left[\frac{\partial\tilde{C}_{11}}{\partial\epsilon}\right]_{\epsilon=0}, \tag{2.121}$$

where from Eq. (1.184)

$$a\tilde{C}_{11} = (\tilde{\alpha}+4\tilde{\sigma}+8\tilde{\mu}+2\tilde{\mu}'+9\tilde{\lambda}'+8\tilde{\lambda}'')\ , \tag{2.122}$$

and in addition to Eqs. (2.84) and (2.109)

$$\tilde{\mu} = \mu + \epsilon\mu^{(1)} \tag{2.123a}$$

$$\tilde{\lambda}'' = \lambda'' + \epsilon\lambda''^{(1)}\ . \tag{2.123b}$$

Using Eqs. (2.121) and (2.122) we obtain

$$\gamma^{(el)}_{LA[100]} = -\frac{1}{6aC_{11}}(\alpha^{(1)}+4\sigma^{(1)}+8\mu^{(1)}+2\mu'^{(1)}+9\lambda'^{(1)}+8\lambda''^{(1)}) , \tag{2.124}$$

and in terms of potential derivatives

$$\gamma^{(el)}_{LA[100]} = -\frac{1}{6aC_{11}}\left[\frac{r_o}{3}\,\phi_1'''(r_o)+\frac{2}{3}\,\phi_1''(r_o)-\frac{2}{3}\,\frac{\phi_1'(r_o)}{r_o}\right.$$
$$+\,4r_2\phi_2'''(r_2)+4\phi_2''(r_2)-\frac{4\phi_2'(r_2)}{r_2}$$
$$+\,\frac{83}{11}\,r_3\phi_3'''(r_3)+\frac{38}{11}\,\phi_3''(r_3)-\frac{38}{11}\,\frac{\phi_3'(r_3)}{r_3}$$
$$\left.+\,8a\phi_4'''(a)-8\sigma\right] . \tag{2.125}$$

Similarly

$$\gamma^{(el)}_{TA[100]} = -\frac{1}{6C_{44}}\left[\frac{\partial\tilde{C}_{44}}{\partial\epsilon}\right]_{\epsilon=0} , \tag{2.126}$$

where from Eq. (1.199)

$$a\tilde{C}_{44} = \tilde{\alpha}+\frac{2}{3}\,\tilde{\sigma}+4\tilde{\mu}+4\tilde{\lambda}+\tilde{\lambda}'+10\tilde{\mu}'+8\tilde{\mu}''$$
$$-\,\frac{(\frac{4}{3}\,\tilde{\sigma}-\tilde{\beta}+2\tilde{\delta}'+3\tilde{\nu}')^2}{(\tilde{\alpha}+\frac{8}{3}\,\tilde{\sigma}+2\tilde{\mu}'+\tilde{\lambda}')} . \tag{2.127}$$

and

$$\tilde{\lambda} = \lambda+\epsilon\lambda^{(1)} \tag{2.128a}$$

$$\tilde{\mu}'' = \mu'' + \epsilon\mu''^{(1)} \tag{2.128b}$$

$$\tilde{\beta} = \beta + \epsilon\beta^{(1)} \tag{2.128c}$$

$$\tilde{\delta}' = \delta' + \epsilon\delta'^{(1)} \tag{2.128d}$$

$$\tilde{\nu}' = \nu' + \epsilon\nu'^{(1)} \; . \tag{2.128e}$$

Differentiating Eq. (2.127) we obtain

$$\gamma^{(el)}_{TA[100]} = - \frac{1}{6aC_{44}} \left[\alpha^{(1)} + \frac{2}{3}\,\sigma^{(1)} + 4\mu^{(1)} + 4\lambda^{(1)} + \lambda'^{(1)} + 10\mu'^{(1)} + 8\mu''^{(1)} - \frac{A}{B}\left(2A^{(1)} - \frac{A}{B}\,B^{(1)}\right) \right], \tag{2.129}$$

where we have defined

$$A = \left(\frac{4}{3}\,\sigma - \beta + 2\delta' + 3\nu'\right) \tag{2.130a}$$

$$B = \left(\alpha + \frac{8}{3}\,\sigma + 2\mu' + \lambda'\right) \tag{2.130b}$$

$$A^{(1)} = \left(\frac{4}{3}\,\sigma^{(1)} - \beta^{(1)} + 2\delta'^{(1)} + 3\nu'^{(1)}\right) \tag{2.130c}$$

$$B^{(1)} = \left(\alpha^{(1)} + \frac{8}{3}\,\sigma^{(1)} + 2\mu'^{(1)} + \lambda'^{(1)}\right) \; . \tag{2.130d}$$

One can rewrite Eq. (2.129) in terms of potential derivatives as

$$\gamma^{(el)}_{TA[100]} = -\frac{1}{6aC_{44}}\left[\begin{aligned}&\frac{r_o}{3}\phi_1'''(r_o)+\frac{2}{3}\phi_1''(r_o)-\frac{2}{3}\frac{\phi_1'(r_o)}{r_o}\\ &+2r_2\phi_2'''(r_2)+6\phi_2''(r_2)-\frac{6\phi_2'(r_2)}{r_2}\\ &+\frac{19}{11}r_3\phi_3'''(r_3)+2\phi_3''(r_3)-\frac{2\phi_3'(r_3)}{r_3}\\ &+8\phi_4''(a)-\frac{8\phi_4'(a)}{a}-\frac{4}{3}\sigma\\ &-\frac{A}{B}(2A^{(1)}-\frac{A}{B}B^{(1)})\end{aligned}\right], \qquad (2.131)$$

with

$$A = \left(\frac{4}{3}\sigma-\frac{1}{3}\phi_1''(r_o)+\frac{\phi_1'(r_o)}{3r_o}+\frac{9}{11}\phi_3''(r_3)-\frac{9\phi_3'(r_3)}{11r_3}\right), \qquad (2.132a)$$

$$B = \left(\frac{1}{3}\phi_1''(r_o)+\frac{2\phi_1'(r_o)}{3r_o}+\phi_3''(r_3)+\frac{2\phi_3'(r_3)}{r_3}+\frac{8}{3}\sigma\right), \qquad (2.132b)$$

$$A^{(1)} = \left[\begin{aligned}&-\frac{r_o}{3}\phi_1'''(r_o)+\frac{1}{3}\phi_1''(r_o)-\frac{\phi_1'(r_o)}{3r_o}+\frac{9}{11}r_3\phi_3'''(r_3)\\ &-\frac{9}{11}\phi_3''+\frac{9\phi_3'(r_3)}{11r_3}-\frac{8}{3}\sigma\end{aligned}\right], \qquad (2.132c)$$

$$B^{(1)} = \left[\begin{aligned}&\frac{r_o}{3}\phi_1'''(r_o)+\frac{2}{3}\phi_1''(r_o)-\frac{2}{3}\frac{\phi_1'(r_o)}{r_o}+r_3\phi_3'''(r_3)\\ &+2\phi_3''(r_3)-\frac{2\phi_3'(r_3)}{r_o}+\frac{16}{3}\sigma\end{aligned}\right]. \qquad (2.132d)$$

At this point it is appropriate to make a few comments. The origin of the negative mode gammas can be understood from Eqs. (2.116) and (2.119). Note that the nearest neighbor third derivative of the potential is not present in Eq. (2.116) but is in Eq. (2.119). Since $\phi_1'''(r_o)$ is of opposite sign to $\phi_1''(r_o)$ for any potential that gets "softer" with increasing distance, the cancellation of $\phi_1'''(r_o)$ in the TAX mode makes this mode gamma extremely likely to be negative. The cancellation of $\phi_1'''(r_o)$ is a direct consequence of the fact that the diamond structure has a nearest neighbor central force instability and the TAX mode is unstable in this case. As we shall see, the modes where cancellation of $\phi_1'''(r_o)$ occurs are the modes that exhibit negative mode gammas. Although the C_{44} "mode" also has a nearest neighbor central force instability, complete cancellation of $\phi_1'''(r_o)$ does not occur in the mode gamma Eq. (2.131) as it does in the unstable modes whose eigenvectors are determined by symmetry.

The important point of the preceeding discussion is to note that crystal structures possessing nearest neighbor central force instabilities should be extremely likely to have negative mode gammas and thus are good candidates for the occurence of negative thermal expansion. Whether or not negative thermal expansion actually occurs will depend on the harmonic phonon spectrum as well as on how many modes exhibit negative mode gammas.

From these considerations we note that several structures can have nearest neighbor central force instabilities. In three dimensions, the simple cubic lattice, the body centered cubic lattice, the hexagonal diamond structure and the graphite structure all have this feature. In two dimensions, the square lattice and triangular coordination or two dimensional "graphite" both exhibit nearest neighbor central force instability. It is also possible to obtain an instability in one dimensional chains of atoms that are allowed to have transverse degrees of freedom.

[110] DIRECTION

As noted in Chapter 1, the Σ_4 mode is the "slow" TA mode in the elastic region. Using Eqs. (1.213) and (1.214) we obtain in the elastic region that

$$\gamma_{\Sigma_4}^{(el)} = -\frac{1}{3a(C_{11}-C_{12})}\left[\begin{array}{l}\alpha^{(1)}-\beta^{(1)}+8\mu^{(1)}-6\nu^{(1)}+11\mu'^{(1)} \\ \\ +21\nu'^{(1)}+4\lambda''^{(1)}+4\mu'^{(1)}+3\sigma^{(1)}\end{array}\right], \tag{2.133}$$

or in terms of potential derivatives

$$\gamma_{\Sigma_4}^{(el)} = -\frac{1}{3a(C_{11}-C_{12})}\left[\begin{array}{l}\phi_1''(r_o)-\frac{\phi_1'(r_o)}{r_o}+r_2\phi_2'''(r_2) \\ +7\phi_2''(r_2)-\frac{7\phi_2'(r_2)}{r_2}+\frac{32}{11}r_3\phi_3'''(r_3) \\ +\frac{89}{11}\phi_3''(r_3)-\frac{89}{11}\frac{\phi_3'(r_3)}{r_3}+4a\phi_4'''(a) \\ +4\phi_4''(a)--\frac{4\phi_4'(a)}{a}-6\sigma\end{array}\right]. \tag{2.134}$$

Note the cancellation of $\phi_1'''(r_o)$ in the above expression. This does not occur for any other modes along symmetry directions in the elastic region. It is also interesting to note that experimentally, the slow TA[110] mode is the only mode along a high symmetry direction that exhibits a negative mode gamma in the elastic region for the diamond structure.[19]

In the course of this work it was necessary to have an analytic expression for the mode gamma of the Σ_3^- mode at the K point. Although the expression is somewhat lengthy, it was found very useful in obtaining a reasonable fit to the available experimental data. Thus we have

$$\gamma_{\Sigma_3^- K} = -\frac{1}{12\omega^2_{\Sigma_3^- K}}\left[\Delta^{(1)} - (\Lambda^2+8\Box^2)^{-\frac{1}{2}}(\Lambda\Lambda^{(1)}+8\Box\Box^{(1)})\right] \qquad (2.135)$$

where

$$\omega^2_{\Sigma_3^- K} = \left[\tfrac{1}{2}\Delta - \tfrac{1}{2}(\Lambda^2+8\Box^2)^{\frac{1}{2}}\right] , \qquad (2.136)$$

and the definitions

$$M\Delta = \left[\begin{array}{l} 8\alpha-(2+\sqrt{2})\beta+(\frac{68}{3}+\sqrt{2})\sigma+(14+6\sqrt{2})\mu \\ +\ 2\nu+(6+2\sqrt{2})\lambda+24\mu'+(46+5\sqrt{2})\nu' \\ +\ 6\mu''+2\lambda'' + \frac{4\pi p_1^2}{\epsilon_s\Omega_o}(-14.706683) \\ +\ \frac{4\pi p_1 p_2}{\epsilon_s\Omega_o}(40.512545) + \frac{4\pi p_2^2}{\epsilon_s\Omega_o}(-18.532303) \end{array}\right] \qquad (2.137)$$

$$M\Delta^{(1)} = \left[\frac{(6-\sqrt{2})}{3} r_o \phi_1'''(r_o) + \frac{(18-\sqrt{2})}{3}\left(\phi_1''(r_o) - \frac{\phi_1'(r_o)}{r_o}\right) \right.$$
$$+ (8+3\sqrt{2}) r_2 \phi_2'''(r_2) + (12+5\sqrt{2})\left(\phi_2''(r_2) - \frac{\phi_2'(r_2)}{r_2}\right)$$
$$+ \frac{(70+5\sqrt{2})}{11} r_3 \phi_3'''(r_3) + \frac{(194-5\sqrt{2})}{11}\left(\phi_3''(r_3) - \frac{\phi_2'(r_2)}{r_3}\right)$$
$$+ 2a\phi_4'''(a) + 6\phi_4''(a) - \frac{6\phi_4'(a)}{a} - \left(\frac{136}{3} + 2\sqrt{2}\right)\sigma$$
$$- \frac{8\pi}{\epsilon_s \Omega_o}\left[(14.706683) p_1 p_1^{(1)} + (18.532303) p_2 p_2^{(1)}\right]$$
$$\left. + \frac{4\pi}{\epsilon_s \Omega_o}(40.512545)\left(p_1 p_2^{(1)} + p_2 p_1^{(1)}\right) \right], \tag{2.138}$$

$$M\Lambda = \left[(4-2\sqrt{2})\alpha - (2+\sqrt{2})\beta + \left(12 - \frac{17\sqrt{2}}{3}\right)\sigma - (2+2\sqrt{2})\mu \right.$$
$$+ 2\nu + (2+2\sqrt{2})\lambda + (4-6\sqrt{2})\mu' + (14-11\sqrt{2})\nu'$$
$$- 2\mu'' + 2\lambda'' + \frac{4\pi p_1^2}{\epsilon_s \Omega_o}(-17.790778)$$
$$\left. + \frac{4\pi p_1 p_2}{\epsilon_s \Omega_o}(26.584681) + \frac{4\pi p_2^2}{\epsilon_s \Omega_o}(-12.350976) \right]. \tag{2.139}$$

$$
M\Lambda^{(1)} = \left[\begin{array}{l}
(2/3-\sqrt{2})r_o\phi_1'''(r_o) + \frac{(10-3\sqrt{2})}{3}(\phi_1''(r_o) - \frac{\phi_1'(r_o)}{r_o}) \\
- \sqrt{2}\ r_2\phi_2'''(r_2)+\sqrt{2}\ \phi_2''(r_2)-\sqrt{2}\ \frac{\phi_2'(r_2)}{r_2} \\
+ \frac{(18-17\sqrt{2})}{11}\ r_3\phi_3'''(r_3) + \frac{(26-49\sqrt{2})}{11}(\phi_3''(r_3) - \frac{\phi_3'(r_3)}{r_3}) \\
+ 2a\phi_4'''(a)-2\phi_4''(a) + \frac{2\phi_4'(a)}{a} + (\frac{34\sqrt{2}}{3} - 24)\sigma \\
- \frac{8\pi}{\epsilon_s\Omega_o}[(17.790778)p_1p_1^{(1)}+(12.350976)p_2p_2^{(1)}] \\
+ \frac{4\pi}{\epsilon_s\Omega_o}(26.584681)(p_1p_2^{(1)}+p_2p_1^{(1)})
\end{array}\right], \tag{2.140}
$$

$$
M\sqsubset = \left[\begin{array}{l}
- \sqrt{2}\ \beta + \frac{2(1+3\sqrt{2})}{3}\ \sigma + (\sqrt{2}-8)\nu' \\
+ \frac{4\pi p_1^2}{\epsilon_s\Omega_o}(-5.6453821) + \frac{4\pi p_1p_2}{\epsilon_s\Omega_o}(8.5753239) \\
+ \frac{4\pi p_2^2}{\epsilon_s\Omega_o}(-5.1730388)
\end{array}\right]. \tag{2.140}
$$

$$
M\Box^{(1)} = \left[\begin{array}{l}
- \frac{\sqrt{2}}{3}(r_o\phi_1'''(r_o)-\phi_1''(r_o) + \frac{\phi_1'(r_o)}{r_o}) \\
+ \frac{(\sqrt{2}-8)}{11}(r_3\phi_3'''(r_3)-\phi_3''(r_3) + \frac{\phi_3'(r_3)}{r_3}) - \frac{4(1+3\sqrt{2})}{3}\ \sigma \\
- \frac{8\pi}{\epsilon_s\Omega_o}[(5.6453821)p_1p_1^{(1)}+(5.1730388)p_2p_2^{(1)}] \\
+ \frac{4\pi}{\epsilon_s\Omega_o}(8.5753239)(p_1p_2^{(1)}+p_2p_1^{(1)})
\end{array}\right]. \tag{2.142}
$$

Note that there is no obvious cancellation of $\phi_1'''(r_o)$ in Eqs. (2.135-2.142). However for silicon we do find a strong reduction of the nearest neighbor third derivative contribution to the mode gamma relative to the nearest neighbor first and second derivative contributions.

[111] DIRECTION

At the L point we find from Eq. (1.237a)

$$\gamma_{LAL} = -\frac{1}{3M\omega^2_{LAL}}\left[3\alpha^{(1)}-2\beta^{(1)}+4\mu^{(1)}+4\nu^{(1)}+2\lambda^{(1)}+2\mu'^{(1)}+\lambda'^{(1)} \right.$$
$$+ 2\nu'^{(1)}-4\delta'^{(1)}+4\mu''^{(1)}2\lambda''^{(1)}+\frac{32}{3}\sigma^{(1)}$$
$$+\frac{4\pi}{\epsilon_s\Omega_o}(3p_1-2p_2)(3p_1^{(1)}-2p_2^{(1)})(T^{22}_{11}(L)+$$
$$\left. + V^{22}_{11}(L))\right], \qquad (2.143)$$

or in terms of potential derivatives

$$\gamma_{LAL} = -\frac{1}{3M\omega^2_{LAL}}\left[\frac{r_o}{3}\phi_1'''(r_o)+\frac{8}{3}\phi_1''(r_o)-\frac{8}{3}\frac{\phi_1'(r_o)}{r_o}\right.$$
$$+4r_2\phi_2'''(r_2)+2\phi_2''(r_2)-\frac{2\phi_2'(r_2)}{r_2}$$
$$+\frac{r_3}{11}\phi_3'''(r_3)+\frac{32}{11}\phi_3''(r_3)-\frac{32}{11}\frac{\phi_3'(r_3)}{r_3}$$
$$+2a\phi_4'''(a)+4\phi_4''(a)-4\frac{\phi_4'(a)}{a}-\frac{64}{3}\sigma$$
$$+\frac{4\pi}{\epsilon_s\Omega_o}(3p_1-2p_2)(3p_1^{(1)}-2p_2^{(1)})(T^{22}_{11}(L)+$$
$$\left. + V^{22}_{11}(L))\right]. \qquad (2.144)$$

Similarly from Eq. (1.237b)

$$\gamma_{LOL} = -\frac{1}{3M\omega_{LOL}^2}\left[\begin{aligned}&\alpha^{(1)}+2\beta^{(1)}+4\mu^{(1)}+4\nu^{(1)}+2\lambda^{(1)}+6\mu'^{(1)}+3\lambda'^{(1)}\\&-2\nu'^{(1)}+4\delta'^{(1)}+4\mu''^{(1)}+2\lambda''^{(1)}\\&+\frac{4\pi}{\epsilon_s\Omega_o}(p_1+2p_2)(p_1^{(1)}+2p_2^{(1)})(T_{11}^{22}(L)-V_{11}^{22}(L))\end{aligned}\right], \tag{2.145}$$

or

$$\gamma_{LOL} = -\frac{1}{3M\omega_{LOL}^2}\left[\begin{aligned}&r_o\phi_1'''(r_o)+4r_2\phi_2'''(r_2)+2\phi_2''(r_2)-\frac{2\phi_2'(r_2)}{r_2}\\&+\frac{43}{11}r_3\phi_3'''(r_3)+\frac{56}{11}\phi_3''(r_3)-\frac{56}{11}\frac{\phi_3'(r_3)}{r_3}\\&+2a\phi_4'''(a)+4\phi_4''(a)-\frac{4\phi_4'(a)}{a}\\&+\frac{4\pi}{\epsilon_s\Omega_o}(p_1+2p_2)(p_1^{(1)}+2p_2^{(1)})(T_{11}^{22}(L)-V_{11}^{22}(L))\end{aligned}\right]. \tag{2.146}$$

For the TA mode we obtain using Eq. (1.241a) that

$$\gamma_{TAL} = -\frac{1}{3M\omega_{TAL}^2}\left[\begin{aligned}&\alpha^{(1)}-\beta^{(1)}+4\mu^{(1)}-2\nu^{(1)}+2\lambda^{(1)}+6\mu'^{(1)}\\&+3\lambda'^{(1)}+\nu'^{(1)}-2\delta'^{(1)}+4\mu''^{(1)}+2\lambda''^{(1)}+3\sigma^{(1)}\\&+\frac{4\pi}{\epsilon_s\Omega_o}(p_1-p_2)(p_1^{(1)}-p_2^{(1)})(V_{12}^{11}(L)-T_{12}^{11}(L))\end{aligned}\right], \tag{2.147}$$

or in terms of potential derivatives

$$\gamma_{TAL} = -\frac{1}{3M\omega_{TAL}^2}\left[\begin{aligned}&\phi_1''(r_o) - \frac{\phi_1'(r_o)}{r_o} + r_2\phi_2'''(r_2) + 5\phi_2''(r_2)\\ &-5\,\frac{\phi_2'(r_2)}{r_2} + \frac{28}{11}\,r_3\phi_3'''(r_3) + \frac{71}{11}\,\phi_3''(r_3)\\ &-\frac{71}{11}\,\frac{\phi_3'(r_3)}{r_3} + 2a\phi_4'''(a) + 4\phi_4''(a)\\ &-4\,\frac{\phi_4'(a)}{a} - 6\sigma\\ &+\frac{4\pi}{\epsilon_s\Omega_o}(p_1-p_2)(p_1^{(1)}-p_2^{(1)})(V_{12}^{11}(L)-T_{12}^{11}(L))\end{aligned}\right]. \tag{2.148}$$

For the TO mode we obtain using Eq. (1.241b) that

$$\gamma_{TOL} = -\frac{1}{3M\omega_{TOL}^2}\left[\begin{aligned}&3\alpha^{(1)}+\beta^{(1)}+4\mu^{(1)}-2\nu^{(1)}+2\lambda^{(1)}+2\mu'^{(1)}\\ &+\lambda'^{(1)}-\nu'^{(1)}+2\delta'^{(1)}+4\mu''^{(1)}+2\lambda''^{(1)}+\frac{17}{3}\sigma^{(1)}\\ &-\frac{2\pi}{\epsilon_s\Omega_o}(3p_1+p_2)(3p_1^{(1)}+p_2^{(1)})(T_{11}^{22}(L)+V_{11}^{22}(L))\end{aligned}\right], \tag{2.149}$$

or in terms of potential derivatives

$$\gamma_{TOL} = -\frac{1}{3M\omega_{TOL}^2}\left[\frac{4}{3}\, r_o\phi_1'''(r_o) + \frac{5}{3}\,\phi_1''(r_o) - \frac{5}{3}\,\frac{\phi_1'(r_o)}{r_o} \right.$$
$$+ r_2\phi_2'''(r_2) + 5\phi_2''(r_2) - 5\,\frac{\phi_2'(r_2)}{r_2}$$
$$+ \frac{16}{11}\, r_3\phi_3'''(r_3) + \frac{17}{11}\,\phi_3''(r_3) - \frac{17}{11}\,\frac{\phi_3'(r_3)}{r_3}$$
$$+ 2a\phi_4'''(a) + 4\phi_4''(a) - 4\,\frac{\phi_4'(a)}{a} - \frac{34}{3}\,\sigma^{(1)}$$
$$\left. - \frac{2\pi}{\epsilon_s\Omega_o}(3p_1+p_2)(3p_1^{(1)}+p_2^{(1)})(T_{11}^{22}(L)+V_{11}^{22}(L))\right]. \tag{2.150}$$

At this point it is interesting to note that $\phi_1'''(r_o)$ is absent from the TAL mode gamma. Experimentally, this mode also has a negative mode gamma.

C-3

ANHARMONIC FIT TO EXPERIMENTAL DATA FOR SILICON

In this section the method used to determine the anharmonic parameters for silicon is described. Using these parameters we then present dispersion curves for the Grüneisen parameters along symmetry directions.

Before proceeding to the anharmonic model used in the present work, we want to discuss two previous anharmonic models used for silicon. The pioneering work of Dolling and Cowley[20] modeled the anharmonic potential energy by a two-body central potential interaction between nearest-neighbors. It was then assumed that two independent parameters could describe the anharmonic interaction and these two parameters were adjusted to give a reasonable fit to the experimentally measured thermal expansion. However, the expression used to compute the mode gammas, Eq. (4.5) of their paper, is incorrect. Their model is also inconsistent in using a shell model for the harmonic properties and a rigid ion model for the anharmonic properties with no connection between the two. Furthermore, it can be shown that nearest-neighbor anharmonicity of any type is in major disagreement with the experimentally measured mode gammas.

The work of Jex[21] was along similar lines to that of Dolling and Cowley but Jex utilized first and second neighbor central potential anharmonicity. Unfortunately, Jex made the approximation of neglecting the first and second derivatives of the potential. This approximation has severe consequences for the mode gammas as can be seen from Eqs. (2.116), (2.134) and (2.148). One of the consequences is that $\phi_2'''(r_2)$ is required to be positive in order to obtain negative mode gammas. Another consequence is that several mode gammas disagree with experiment by more than a factor of two. Jex concluded that $\phi_2'''(r_2)$ was more than a thousand times smaller in magnitude than $\phi_1'''(r_o)$, thus seemingly justifying his assumption of only first and second neighbor anharmonicity. However, using our analytic expressions with the approximation of Jex, it is easy to show that the values of the mode gammas obtained by Jex are inconsistent with his small value of $\phi_2'''(r_2)$. Based on the above considerations, we seriously question the linewidth calculation of Jex as well. Furthermore, one can show that more general second neighbor anharmonicity is unable to give reasonable agreement with the experimentally measured mode gammas.

In the present calculation, we have used the ten parameter harmonic model of Chapter 1 together with six independent parameters for the anharmonic model. The six independent parameters are $\phi_1'''(r_o)$, $\phi_2'''(r_2)$, $\phi_3'''(r_3)$, $\phi_4'''(a)$, $p_1^{(1)}$ and $p_2^{(1)}$. These parameters were obtained by performing a weighted, linear, least square fit to the following experimental data γ_{RA} , γ_{TAX} , γ_{TOX} , γ_{TAL} , γ_{TOL} , $\gamma^{(el)}_{LA[100]}$, $\gamma^{(el)}_{TA[100]}$, $\gamma_{\Sigma_3^-}$ K and $\gamma^{(el)}_{\Sigma_4}$. The experimental values of these mode gammas are listed in Table 5. In Table 6 we list the values of the anharmonic parameters determined from this fitting procedure. Note the rapid fall off of the third order potential derivatives by the fourth neighbor distance, though not as rapid as the fall off of the second order potential derivatives in Table 4. In Fig. 10 we have plotted the mode gammas along symmetry directions for this model. These curves are a marked improvement over those of Jex. Though the agreement with experiment is at worst 35%, most of the modes are much better and considering the large uncertainties in the experimental data this is not too bad. Note that the mode gammas reflect the same difficulty found in the harmonic dispersion curves, namely, the dipole model produces considerably more lowering of the mode gamma at the X point than at the L point. This causes the mode gamma at L to be less negative than experiment and the mode gamma at X to be more negative than experiment.

TABLE 5

Experimental values of mode Grüneisen parameters for silicon.[22] Elastic mode gammas determined from the pressure dependence of the elastic constants.

$\gamma_{RA} = .98 \pm .06$

$\gamma_{TAX} = -1.4 \pm .3$

$\gamma_{TOX} = 1.5 \pm .1$

$\gamma_{TAL} = -1.3 \pm .3$

$\gamma_{TOL} = 1.3 \pm .2$

$\gamma_{\Sigma_4 K} = -1.0 \pm .3$

$\gamma_{\Sigma_3^- K} = -.3 \pm .1$

$\gamma^{(el)}_{LA[100]} = 1.11$

$\gamma^{(el)}_{TA[100]} = .325$

$\gamma^{(el)}_{\Sigma_4} = -.1$

TABLE 6

Anharmonic parameters for silicon determined by the method described in the text. $p_1^{(1)} = z_1^{(1)}e$ and $p_2^{(1)} = z_2^{(1)}e$ where e is the magnitude of the electron charge in C.G.S. units.

$$\phi_1'''(r_o) = -\ 4.5272\times10^{13}\,\mathrm{dyne/cm^2}$$

$$\phi_2'''(r_2) = -\ 2.3833\times10^{12}$$

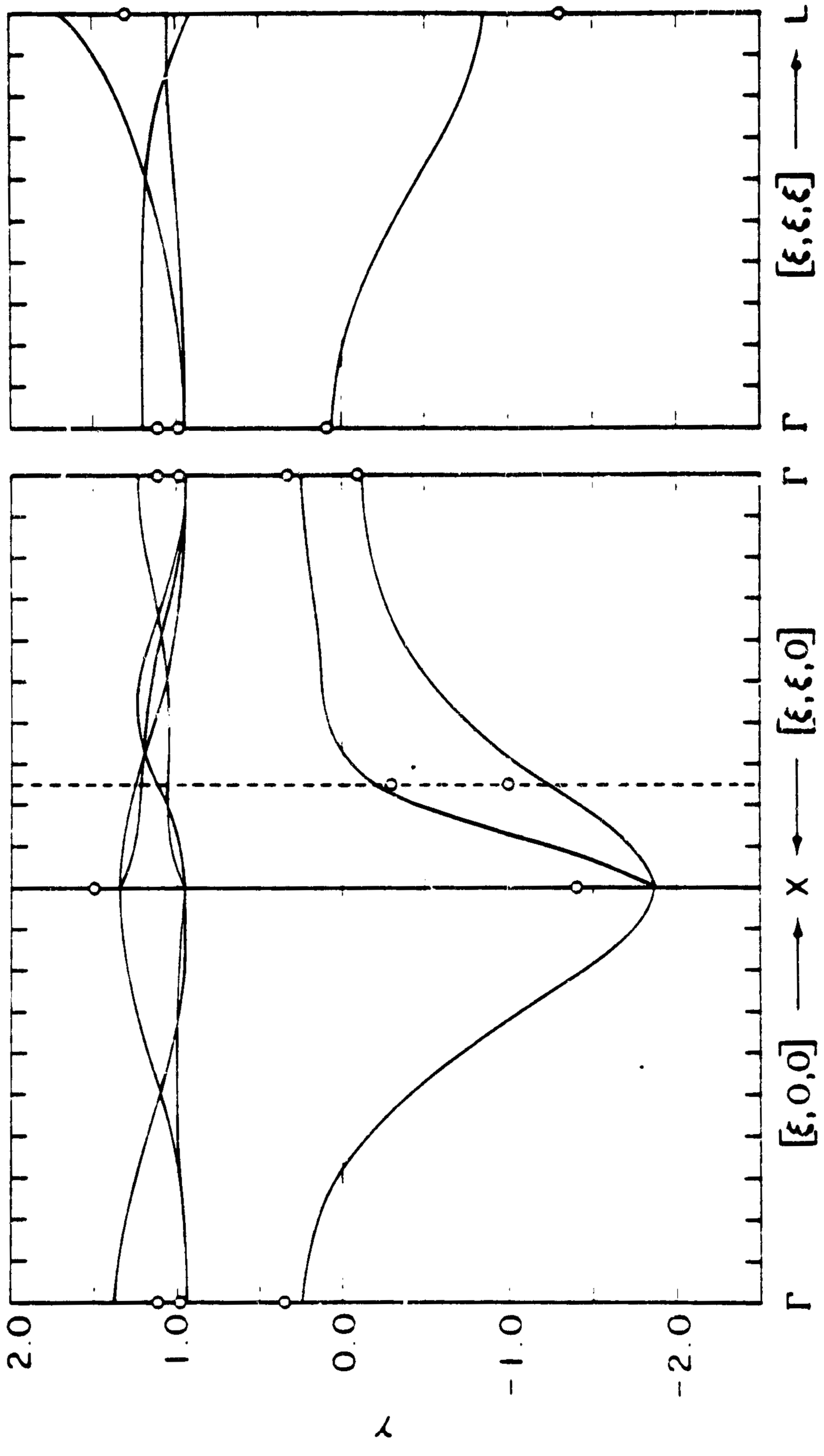
$$\phi_3'''(r_3) = \ 6.8387\times10^{11}$$

$$\phi_4'''(a) = -\ 4.9468\times10^{11}$$

$$z_1^{(1)} = -\ 0.405426 \qquad z_2^{(1)} = 0.608139$$

$$\sigma^{(1)} = -\ 2\sigma$$

Figure 10. Mode gammas for silicon along symmetry directions using the model described in the text (solid lines). Circles are experimental data.


γ
2.0
1.0
0.0
-1.0
-2.0
Γ
[ξ,0,0]
X
[ξ,ξ,0]
Γ
Γ
[ξ,ξ,ξ]
L

CALCULATION OF THERMAL EXPANSION FOR SILICON

Having obtained the model parameters, we can use Eq. (2.59) to calculate the thermal expansion coefficient. The sum over the first Brillouin zone of the crystal is the major difficulty in carrying out this procedure. Several numerical methods have been developed to evaluate such sums.[23] In the interest of maximum computing efficiency, we have chosen the special $\vec{k}$ point method of Chadi and Cohen.[24] Briefly, this method evaluates sums over the Brillouin zone by

$$\sum_{\vec{k}}^{BZ} f(\vec{k}) \cong N \sum_{i=1}^{n} \alpha_i f(\vec{k}_i) \ , \qquad (2.151)$$

with

$$\sum_{i=1}^{n} \alpha_i = 1 \ . \qquad (2.152)$$

Here $f(\vec{k})$ is a smoothly varying function of wavevector, N is the number of unit cells of the crystal, $\vec{k}_i$ are the special $\vec{k}$ points, α_i the associated weighting factors and n is the number of special $\vec{k}$ points used. As the number of special $\vec{k}$ points increases, the approximation, Eq. (2.151), improves. In the present study we have investigated the case of 10 special $\vec{k}$ points and 60 special $\vec{k}$ points. These special points are all in the irreducible 1/48th sector of the Brillouin zone and are equivalent to 256 points and 2048 points respectively in the full zone.

The 60 special $\vec{k}$ points and associated weights for the fcc lattice were obtained from D.J. Chadi[25] and are listed in Table 7 for reference purposes.

A computer program was written to compute the frequencies and mode gammas for a general $\vec{k}$ point. The thermal expansion was calculated as well as the thermal strain ϵ given by

$$\epsilon = \frac{\hbar}{3B_o V_o} \sum_{\vec{k}j}^{BZ} \omega(\vec{k}j)\gamma(\vec{k}j)(\bar{n}_{\vec{k}j} + \frac{1}{2}) \ . \qquad (2.153)$$

The results of these calculations for 10 special $\vec{k}$ points are presented in Table 8 and for 60 special $\vec{k}$ points in Table 9. The thermal expansion coefficient is plotted in Figs. 11 and 12 for the calculation using 60 $\vec{k}$ points.

As can be seen from Figs. 11 and 12, the agreement with experiment is good from 17K to 700K . The deviations below 17K are attributed to two sources. First, the experimental points at low temperatures are subject to large uncertainties due to the fact that the thermal expansion coefficient is getting extremely small. Second, we suspect that the inclusion of more than 60 special $\vec{k}$ points will raise the theoretical curve below 17K . We suspect this because the calculation with 10 $\vec{k}$ points was raised considerably below 17K by going to 60 $\vec{k}$ points. The deviation from experiment near 70K is attributed to the fact that our fit to the TAL mode gamma is not negative enough. As can be seen, theory and experiment are in good agreement to 700K , at which point the two depart. Note that the Debye temperature for silicon is 645K [28] and the melting point is 1687K.[29] However, even at 1600K , the difference between theory and experiment is only 12%. Considering the approximate fit of our mode gammas we consider this good agreement.

In our calculations to this point, the bulk modulus was taken as temperature independent. A softening of the bulk modulus with increasing temperature would raise the theoretical curve and improve agreement with experiment. We can estimate this effect by using the quasiharmonic bulk modulus given by

$$\tilde{B} = B + \epsilon B^{(1)} , \tag{2.154}$$

with

$$B^{(1)} = \frac{1}{3a}\left[\begin{array}{l} 4\beta^{(1)} - \alpha^{(1)} + 16\nu^{(1)} - 8\lambda^{(1)} - 11\mu'^{(1)} \\ + 132\nu'^{(1)} + 8\lambda''^{(1)} - 16\mu''^{(1)} \end{array}\right] . \tag{2.155}$$

and B given by Eq. (1.217). The dashed curve in Fig. 12 is obtained by multiplying the solid curve by the correction factor $\tilde{B}(300K)/\tilde{B}(T)$. Note the improved agreement that results from taking this temperature dependence of the bulk modulus into account so that now the theory and experiment are within 5% at 1600K . However, it is not unreasonable to suggest that at these high temperatures higher order anharmonic effects could be playing a role or even other contributions to the free energy, such as the thermal creation of imperfections. It appears that these effects are quite small for silicon.

As a final remark, we can combine Eqs. (2.53) and (2.54) to obtain

$$P_o = 3B_o\epsilon_o \ , \tag{2.156}$$

where B_o is the bare bulk modulus, ϵ_o the zero-point strain and P_o the zero-point phonon pressure. Using ϵ_o from Table 9 and from Table 3

$$B_o = 9.5847\times10^{11}\text{dyne/cm}^2 \ , \tag{2.157}$$

we obtain

$$P_o = 4.433 \text{ kbar} \ . \tag{2.158}$$

As mentioned earlier, P_o is the pressure required to make the strain zero at $T = 0$. It is a purely quantum mechanical effect and is a result of allowing the atoms to move in an anharmonic potential. This should be taken into account in calculations of the phase transition pressure of silicon from the diamond structure to the β-tin structure. Such calculations are performed with the atoms motionless. Although zero-point corrections to the total energy are made, to the author's knowledge, this is the first calculation of the size of the zero-point contribution to the pressure. Note that the calculations of Yin and Cohen[30] gave a phase transition pressure of 99kbar and the experimental value is 125kbar. The zero-point pressure of 4.4kbar is interesting in light of this difference. It is an additional pressure that is required to be applied in order to have the same volume for a given pressure as if the atoms were all at rest, thus tending to raise the calculated transition pressure. However, to be conclusive, one should also calculate the zero-point phonon pressure for silicon in the β-tin structure as well.

TABLE 7

60 special $\vec{k}$ points for the fcc lattice in units of $\left(\frac{1}{16}\right)\frac{2\pi}{a}$. (Courtesy D.J. Chadi)

(1, 1,1) , (3, 1,1) , (5, 1,1) , (7, 1,1) , (9, 1,1) ,
(11, 1,1) , (13, 1,1) , (15, 1,1) , (3, 3,1) , (5, 3,1) ,
(7, 3,1) , (9, 3,1) , (11, 3,1) , (13, 3,1) , (15, 3,1) ,
(5, 5,1) , (7, 5,1) , (9, 5,1) , (11, 5,1) , (13, 5,1) ,
(15, 5,1) , (7, 7,1) , (9, 7,1) , (11, 7,1) , (13, 7,1) ,
(15, 7,1) , (9, 9,1) , (11, 9,1) , (13, 9,1) , (11,11,1) ,
(3, 3,3) , (5, 3,3) , (7, 3,3) , (9, 3,3) , (11, 3,3) ,
(13, 3,3) , (15, 3,3) , (5, 5,3) , (7, 5,3) , (9, 5,3) ,
(11, 5,3) , (13, 5,3) , (15, 5,3) , (7, 7,3) , (9, 7,3) ,
(11, 7,3) , (13, 7,3) , (9, 9,3) , (11, 9,3) , (5, 5,5) ,
(7, 5,5) , (9, 5,5) , (11, 5,5) , (13, 5,5) , (7, 7,5) ,
(9, 7,5) , (11, 7,5) , (7, 7,7) , (9, 7,7) , (9, 9,5) ,

Associated weights

(x,x,x) points $\alpha = 1/256$
(x,y,y) points $\alpha = 3/256$
(x,y,z) points $\alpha = 6/256$

TABLE 8

Volume thermal expansion coefficient and thermal strain for silicon using 10 special $\vec{k}$ points

T (K)	α (K^{-1})	ε ($\times 10^3$)
0	0	1.54173
5	-1.81734×10^{-13}	"
6	-1.94981×10^{-12}	"
7	-1.01301×10^{-11}	"
8	-3.37142×10^{-11}	"
9	-8.40683×10^{-11}	"
10	-1.73045×10^{-10}	"
11	-3.13907×10^{-10}	"
12	-5.25860×10^{-10}	"
13	-8.40982×10^{-10}	"
14	-1.31147×10^{-9}	"
15	-2.01518×10^{-9}	"
16	-3.05801×10^{-9}	"
17	-4.57273×10^{-9}	"
18	-6.71433×10^{-9}	1.54172
19	$-9.6528\ \times10^{-9}$	"
20	-1.35649×10^{-8}	"
21	-1.86243×10^{-8}	1.54171
22	-2.49942×10^{-8}	1.54171
23	-3.28196×10^{-8}	1.54170
24	-4.22219×10	1.54168

TABLE 8 (cont.)

T (K)	α (K^{-1})	ϵ ($\times 10^3$)
25	-5.32952×10^{-8}	1.54167
30	-1.34971×10^{-7}	1.54152
35	-2.56732×10^{-7}	1.54120
40	-4.05310×10^{-7}	1.54065
45	-5.64063×10^{-7}	1.53984
50	-7.17923×10^{-7}	1.53877
55	-8.55092×10^{-7}	1.53745
60	-9.67052×10^{-7}	1.53593
65	-1.04804×10^{-6}	1.53425
70	-1.09450×10^{-6}	1.53246
75	-1.10464×10^{-6}	1.53062
80	-1.07810×10^{-6}	1.52880
85	-1.01569×10^{-6}	1.52705
90	-9.19105×10^{-7}	1.52543
95	-7.90721×10^{-7}	1.52400
100	-6.33396×10^{-7}	1.52281
110	-2.44648×10^{-7}	1.52132
120	2.21055×10^{-7}	1.52126
130	7.38850×10^{-7}	1.52285
140	1.28710×10^{-6}	1.52622
150	1.84817×10^{-6}	1.53145
160	2.40845×10^{-6}	1.53854
170	2.95791×10^{-6}	1.54749

TABLE 8 (cont.)

T (K)	α (K^{-1})	ϵ ($\times 10^3$)
180	3.48954×10^{-6}	1.55824
190	3.99872×10^{-6}	1.57073
200	4.48268×10^{-6}	1.58487
210	4.94002×10^{-6}	1.60059
220	5.37036×10^{-6}	1.61778
230	5.77401×10^{-6}	1.63636
240	6.15176×10^{-6}	1.65624
250	6.50470×10^{-6}	1.67734
260	6.83412×10^{-6}	1.69958
270	7.14139×10^{-6}	1.72288
280	7.42792×10^{-6}	1.74717
290	7.69511×10^{-6}	1.77238
300	7.94432×10^{-6}	1.79845
350	8.96355×10^{-6}	1.93983
400	9.69659×10^{-6}	2.09565
450	1.02353×10^{-5}	2.26197
500	1.06401×10^{-5}	2.43609
550	1.09505×10^{-5}	2.61612
600	1.11932×10^{-5}	2.80073
650	1.13860×10^{-5}	2.98895
700	1.15415×10^{-5}	3.18006
750	1.16687×10^{-5}	3.37351
800	1.17739×10^{-5}	3.56889

TABLE 8 (cont.)

T (K)	α (K^{-1})	ϵ ($\times 10^3$)
850	1.18619×10^{-5}	3.76588
900	1.19361×10^{-5}	3.96421
950	1.19994×10^{-5}	4.16369
1000	1.20537×10^{-5}	4.36414
1050	1.21006×10^{-5}	4.56544
1100	1.21414×10^{-5}	4.76746
1150	1.21772×10^{-5}	4.97012
1200	1.22087×10^{-5}	5.17334
1250	1.22365×10^{-5}	5.37706
1300	1.22613×10^{-5}	5.58121
1350	1.22834×10^{-5}	5.78575
1400	1.23032×10^{-5}	5.99064
1450	1.23210×10^{-5}	6.19585
1500	1.23371×10^{-5}	6.40133
1550	1.23517×10^{-5}	6.60708
1600	1.23650×10^{-5}	6.81305
1650	1.23770×10^{-5}	7.01924
1700	1.23881×10^{-5}	7.22561

TABLE 9

Volume thermal expansion coefficient and thermal strain for silicon using 60 special $\vec{k}$ points.

T (K)	α (K^{-1})	ϵ ($\times 10^{3}$)
0	0	1.54184
5	1.41794×10^{-11}	"
6	4.28023×10^{-11}	"
7	9.65599×10^{-11}	"
8	1.86983×10^{-10}	"
9	3.28359×10^{-10}	"
10	5.31819×10^{-10}	"
11	7.97764×10^{-10}	"
12	1.10894×10^{-9}	"
13	1.424472×10^{-9}	"
14	1.67673×10^{-9}	"
15	1.76651×10^{-9}	"
16	1.56576×10^{-9}	"
17	9.19612×10^{-10}	"
18	-3.47348×10^{-10}	"
19	-2.42303×10^{-9}	"
20	-5.49874×10^{-9}	"
21	-9.76004×10^{-9}	"
22	-1.53785×10^{-8}	"
23	-2.25047×10^{-8}	1.54183
24	-3.12632×10^{-8}	1.54182

TABLE 9 (cont.)

T (K)	α (K^{-1})	ϵ ($\times 10^3$)
25	-4.17490×10^{-8}	1.54181
30	-1.21275×10^{-7}	1.54168
35	-2.41884×10^{-7}	1.54138
40	-3.89885×10^{-7}	1.54086
45	-5.48352×10^{-7}	1.54008
50	-7.02070×10^{-7}	1.53903
55	-8.39167×10^{-7}	1.53775
60	-9.51091×10^{-7}	1.53625
65	-1.03206×10^{-6}	1.53459
70	-1.07851×10^{-6}	1.53283
75	-1.08864×10^{-6}	1.53102
80	-1.06211×10^{-6}	1.52922
85	-9.99695×10^{-7}	1.52750
90	-9.03106×10^{-7}	1.52591
95	-7.74721×10^{-7}	1.52450
100	-6.17395×10^{-7}	1.52334
110	-2.28646×10^{-7}	1.52191
115	-3.79891×10^{-9}	1.52171
120	2.37060×10^{-7}	1.52190
130	7.54856×10^{-7}	1.52354
140	1.30311×10^{-6}	1.52697
150	1.86418×10^{-6}	1.53224
160	2.42446×10^{-6}	1.53939

TABLE 9 (cont.)

T (K)	α (K^{-1})	ϵ ($\times 10^3$)
170	2.97393×10^{-6}	1.54840
180	3.50556×10^{-6}	1.55920
190	4.01473×10^{-6}	1.57174
200	4.49869×10^{-6}	1.58594
210	4.95604×10^{-6}	1.60170
220	5.38638×10^{-6}	1.61895
230	5.79003×10^{-6}	1.63758
240	6.16777×10^{-6}	1.65752
250	6.52071×10^{-6}	1.67867
260	6.85013×10^{-6}	1.70096
270	7.15740×10^{-6}	1.72432
280	7.44393×10^{-6}	1.74866
290	7.71112×10^{-6}	1.77392
300	7.96033×10^{-6}	1.80004
350	8.97955×10^{-6}	1.94169
400	9.71260×10^{-6}	2.09778
450	1.02513×10^{-5}	2.26437
500	1.06561×10^{-5}	2.43875
550	1.09665×10^{-5}	2.61905
600	1.12092×10^{-5}	2.80393
650	1.14020×10^{-5}	2.99241
700	1.15575×10^{-5}	3.18379

TABLE 9 (cont.)

T (K)	α (K^{-1})	ϵ ($\times 10^3$)
750	1.16847×10^{-5}	3.37751
800	1.17899×10^{-5}	3.57316
850	1.18779×10^{-5}	3.77041
900	1.19521×10^{-5}	3.96901
950	1.20154×10^{-5}	4.16875
1000	1.20697×10^{-5}	4.36947
1050	1.21166×10^{-5}	4.57103
1100	1.21574×10^{-5}	4.77333
1150	1.21932×10^{-5}	4.97625
1200	1.22247×10^{-5}	5.17974
1250	1.22525×10^{-5}	5.38372
1300	1.22773×10^{-5}	5.58814
1350	1.22994×10^{-5}	5.79295
1400	1.23192×10^{-5}	5.99811
1450	1.23370×10^{-5}	6.20358
1500	1.23531×10^{-5}	6.40933
1550	1.23677×10^{-5}	6.61534
1600	1.23809×10^{-5}	6.82158
1650	1.23930×10^{-5}	7.02803
1700	1.24041×10^{-5}	7.23468

Figure 11. Volume thermal expansion coefficient for silicon calculated using 60 special $\vec{k}$ points (solid line). Circles are experimental data (Ref. 26).

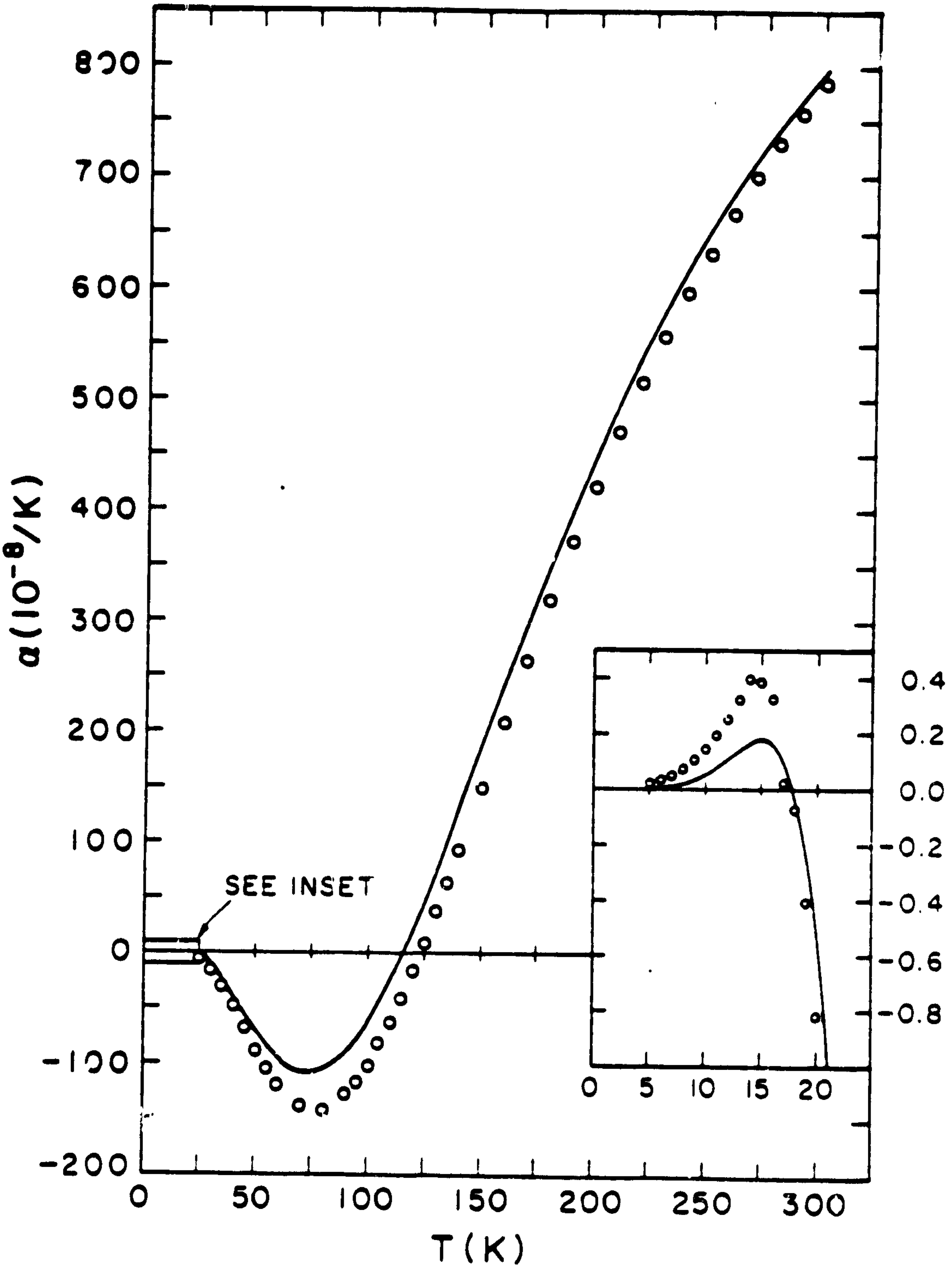
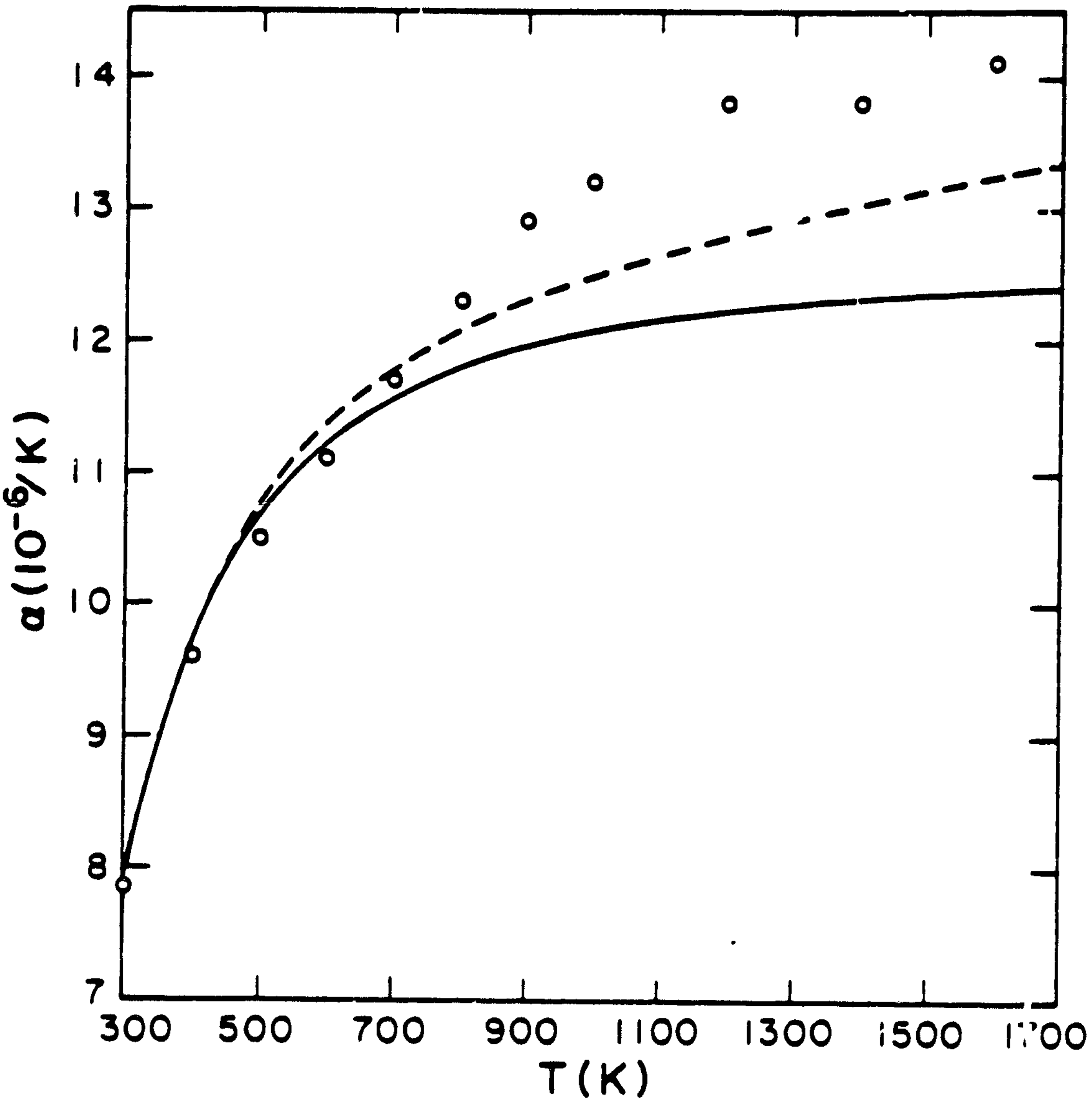

800
700
600
500
400
300
200
100
0
-100
-200
$\alpha(10^{-8}/K)$
SEE INSET
0
50
100
150
200
250
300
T(K)
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
0
5
10
15
20

Figure 12. Volume thermal expansion coefficient for silicon calculated using 60 special $\vec{k}$ points (solid line). Circles are experimental data (Ref. 27). The dashed line is calculated by applying a quasiharmonic correction to the bulk modulus. The Debye temperature for silicon is 645K and the melting point is 1687K .


14
13
12
11
10
9
8
7
300
500
700
900
1100
1300
1500
1700
$\alpha(10^{-6}/K)$
T(K)

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Chapter 3

Anomalous Thermoelastic Effect in Silicon

> "For God so loved the world,
> that he gave his only
> begotten Son, that whosoever
> believeth in him should
> not perish, but have everlasting life."
>
> John 3:16

In this chapter the equations of visco and thermoelasticity are discussed and the dispersion relation for a cubic material presented. The thermoelastic contribution to the acoustic attenuation in silicon is computed from 1-300K . Strong attenuation anomalies associated with negative thermal expansion are found in the vicinity of 17K and 125K . Comparison with experimental results is discussed. It is suggested that anharmonic effects are responsible for the anomalies seen in low frequency measurements and that several materials should exhibit similar behaviour.

Various studies of acoustic attenuation in silicon have been carried out in the past several years. Measurements of acoustic attenuation at relatively high frequencies have been made by Mason and Bateman[1], who studied silicon and germanium at 300 - 500 MHz and found that the attenuation went smoothly to very low values at low temperatures. A quantity which affects the acoustic attenuation is the viscosity tensor, whose elements have been determined by Helme and King[2] for silicon at 1 GHz and 300K . On the other hand, measurements at low frequencies indicate attenuation anomalies. McGuigan *et al.*[3] measured the mechanical Q of a large single crystal of silicon at 20 KHz and observed attenuation anomalies at 13K and 115K . Davis[4] has also observed a dip in Q near 13K at 3.4 KHz in a large single crystal of silicon. McGuigan *et al.* attribute the anomalies to impurities and mechanical imperfections of the crystal. However, no conclusive evidence is presented for this mechanism, and it is possible that the effect is an intrinsic property. It is the purpose of this investigation to show that anharmonic attenuation can very rapidly in a narrow range of temperature and exhibits anamalies near 13K and 125K in silicon.

Consider the combined thermoelastic and viscoelastic effects in a cubic crystal. The equations of motion are[5,6]

$$\begin{aligned}\rho \frac{\partial^2 u_x}{\partial t^2} = &- B\alpha \frac{\partial T}{\partial x} + \left(C_{11} + \eta_{11} \frac{\partial}{\partial t}\right)\frac{\partial^2 u_x}{\partial x^2} + \\ &+ \left(C_{44} + \eta_{44} \frac{\partial}{\partial t}\right)\left(\frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2}\right) + \\ &+ \left(C_{12} + \eta_{12} \frac{\partial}{\partial t} + C_{44} + \eta_{44} \frac{\partial}{\partial t}\right)\left(\frac{\partial^2 u_y}{\partial x \partial y} + \frac{\partial^2 u_z}{\partial x \partial z}\right)\end{aligned} \tag{3.1a}$$

$$\rho \frac{\partial^2 u_y}{\partial t^2} = - B\alpha \frac{\partial T}{\partial y} + (C_{11} + \eta_{11} \frac{\partial}{\partial t}) \frac{\partial^2 u_y}{\partial y^2} + (C_{44} + \eta_{44} \frac{\partial}{\partial t}) \times$$

$$\times \left(\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial z^2} \right) + (C_{12} + \eta_{12} \frac{\partial}{\partial t} + C_{44} + \eta_{44} \frac{\partial}{\partial t}) \times$$

$$\times \left(\frac{\partial^2 u_x}{\partial y \partial x} + \frac{\partial^2 u_z}{\partial y \partial z} \right) \qquad (3.1b)$$

$$\rho \frac{\partial^2 u_z}{\partial t^2} = - B\alpha \frac{\partial T}{\partial z} + (C_{11} + \eta_{11} \frac{\partial}{\partial t}) \frac{\partial^2 u_z}{\partial z^2} + (C_{44} + \eta_{44} \frac{\partial}{\partial t}) \times$$

$$\times \left(\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} \right) + (C_{12} + \eta_{12} \frac{\partial}{\partial t} + C_{44} + \eta_{44} \frac{\partial}{\partial t}) \times$$

$$\times \left(\frac{\partial^2 u_x}{\partial z \partial x} + \frac{\partial^2 u_y}{\partial z \partial y} \right) \qquad (3.1c)$$

while the heat equation is[6]

$$C_v \frac{\partial T}{\partial t} + \frac{(C_p - C_v)}{\alpha} \frac{\partial}{\partial t}(\nabla \cdot \vec{u}) = \kappa \nabla^2 T \ . \qquad (3.2)$$

Here ρ is the mass density, C_{ij} and η_{ij} are the elastic moduli and viscosity tensor elements respectively, B is the isothermal bulk modulus, α is the coefficient of volume thermal expansion, T is the temperature, C_p and C_v are the heat capacity per unit volume at constant pressure and volume respectively, κ is the thermal conductivity, and the u_i are the cartesian components of the elastic displacement.

We seek plane wave solutions to Eqs. (3.1) and (3.2) of the form

$$u_i = u_{io}\, e^{i\vec{k}\cdot\vec{x}-i\omega t} \tag{3.3}$$

$$T = T_o + T_1\, e^{i\vec{k}\cdot\vec{x}-i\omega t} \tag{3.4}$$

where $\vec{k}$ is the wavevector and ω is the frequency. For simplicity, we specialize to a longitudinal wave propagating in the [111] direction. Substituting Eqs. (3.3) and (3.4) into Eqs. (3.1) and (3.2) we find that the dispersion relation is

$$k_{\pm}^2 = \frac{a}{(1-i\omega\tau)} + i\left(b + \frac{c}{1-i\omega\tau}\right) \pm \left\{\left[\frac{a}{(1-i\omega\tau)} + i\left(b + \frac{c}{1-i\omega\tau}\right)\right]^2 - \frac{4iab}{(1-i\omega\tau)}\right\}^{\frac{1}{2}} \tag{3.5}$$

where we have defined $|\vec{k}| = k$ and

$$a = \frac{\omega^2}{2v_o^2}\ ,\quad b = \frac{\omega C_v}{2\kappa}\ ,\quad c = \frac{B^2\alpha^2 T\omega}{2\rho\kappa v_o^2} \tag{3.6}$$

$$v_o = \left(\frac{C_{11}+2C_{12}+4C_{44}}{3\rho}\right)^{\frac{1}{2}} \tag{3.7}$$

$$\tau = \left(\frac{\eta_{11}+2\eta_{12}+4\eta_{44}}{C_{11}+2C_{12}+4C_{44}}\right)\ . \tag{3.8}$$

The lower sign in Eq. (3.5) corresponds to the elastic mode while the upper sign corresponds to the thermal mode. Note that Eq. (3.5) is valid for any purely longitudinal wave, provided we use the appropriate velocity v_o and viscous relaxation time τ for the direction of propagation. Also note that τ here is not the thermal relaxation time.

Various cases of Eq. (3.5) are of interest. For a pure viscoelastic effect we have

$$k^2 = \frac{\omega^2}{v_o^2(1-i\omega\tau)} \quad . \tag{3.9}$$

This can be obtained from Eq. (3.5) by putting α equal to zero. Letting

$$k = k_1 + ik_2 \tag{3.10}$$

we obtain for $\omega\tau<<1$

$$k_1 = \frac{\omega}{v_o} \tag{3.11}$$

$$k_2 = \frac{\omega^2\tau}{2v_o} \quad . \tag{3.12}$$

Note that $\omega\tau<<1$ is satisfied in silicon at room temperature even at 1 GHz .

For the pure thermoelastic effect $\tau = 0$. This dispersion relation has been obtained previously,[7] and in the case that b>>a,c we have

$$k_2 = \frac{\kappa B^2 \alpha^2 T \omega^2}{2 \rho v_o^5 C_v^2} \qquad (3.13)$$

and k_1 is given by Eq. (3.11). Equation (3.13) is the usual result,[1] and applies to silicon at 20 KHz from 1 - 300K .

For combined thermo and viscoelastic effects, one may show by expanding the dispersion relation (3.5) that in the case b>>a,c and $\omega\tau << 1$, k_1 is given by Eq. (3.11) and

$$k_2 = \frac{\omega^2 \tau}{2 v_o} + \frac{\kappa B^2 \alpha^2 T \omega^2}{2 \rho v_o^5 C_v^2} \ . \qquad (3.14)$$

The usual situation is that the second term of Eq. (3.14) is only a few percent of the first term.

Since the temperature dependence of the viscosity tensor elements has not been measured at low frequency over a range of temperature and has not been calculated using a realistic phonon model for silicon, we focus on the thermoelastic contribution to the attenuation. Using data found in the literature,[8-10] we have evaluated Eq. (3.13) for silicon in the range of 1-300K at 20 KHz . These results are presented in Table 10. Figure 13 is a plot of these results. Figure 14 is an expanded version of the region from 1-50K . Note that the plots are normalized to be independent of frequency in the range of validity of Eq. (3.13).

The attenuation shows rather marked features. The maximum at 14K is associated with the thermal expansion coefficient passing through a maximum near 14K . The dip near 17K is associated with the thermal expansion coefficient going through zero and changing sign. The broad peak from 35 - 60K is due to the combined factors of the thermal conductivity passing through its maximum and decreasing, while the magnitude of the expansion coefficient increases. The slight shoulder in the curve from 70 - 80K is due to the thermal expansion coefficient passing through its minimum negative value. The dip in attenuation near 125K is due to the thermal expansion coefficient changing sign from negative to positive in this region. Note that the maximum thermoelastic attenuation occurs in the vicinity of 40 - 45K and not at room temperature. In fact, the thermoelastic attenuation at 40K is more than a factor of 3 times greater than it is at room temperature. In this region we expect the thermoelastic effect to be more than a few percent of the total attenuation for longitudinal waves. Careful measurements of the viscosity tensor elements at low frequency are necessary to substantiate this conclusion.

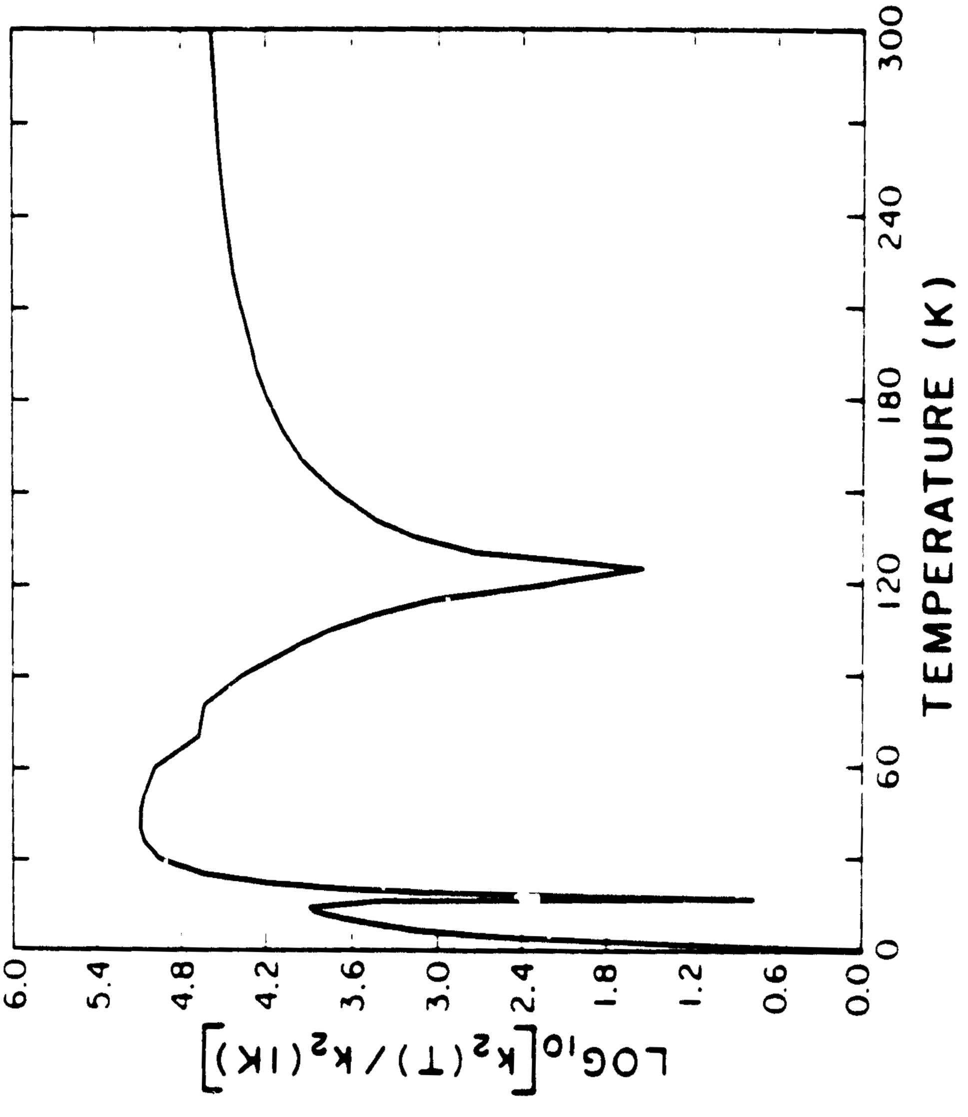
The existence of thermoelastic attenuation anomalies near the temperatures at which McGuigan et al.[3] and Davis[4] observed anomalies in the mechanical Q suggests that anharmonic effects are the cause of the latter anomalies and not impurities or mechanical imperfections in the crystal. Indeed, the sample of McGuigan et al. was boron doped with a concentration of 3×10^{15} boron atoms/cm^3, while the sample of Davis had a boron concentration of 8×10^{14} atoms/cm^3, both of which are rather low impurity concentrations. In order to settle the question, it is necessary to perform experiments on extremely pure samples and see if the anomalies persist. If they do, one would have very strong evidence in favor of the anharmonicity mechanism. Furthermore, since several semiconductors such as Ge, GaAs, ZnS, ZnSe and CdTe exhibit negative thermal expansion,[11] one may expect that they also will have anomalous acoustic attenuation if, in fact, the effect is intrinsic.

TABLE 10

Values of k_2 for silicon at 20 KHz along the [111] direction using Eq. (3.13). Units of k_2 are 10^{-12}/meter.

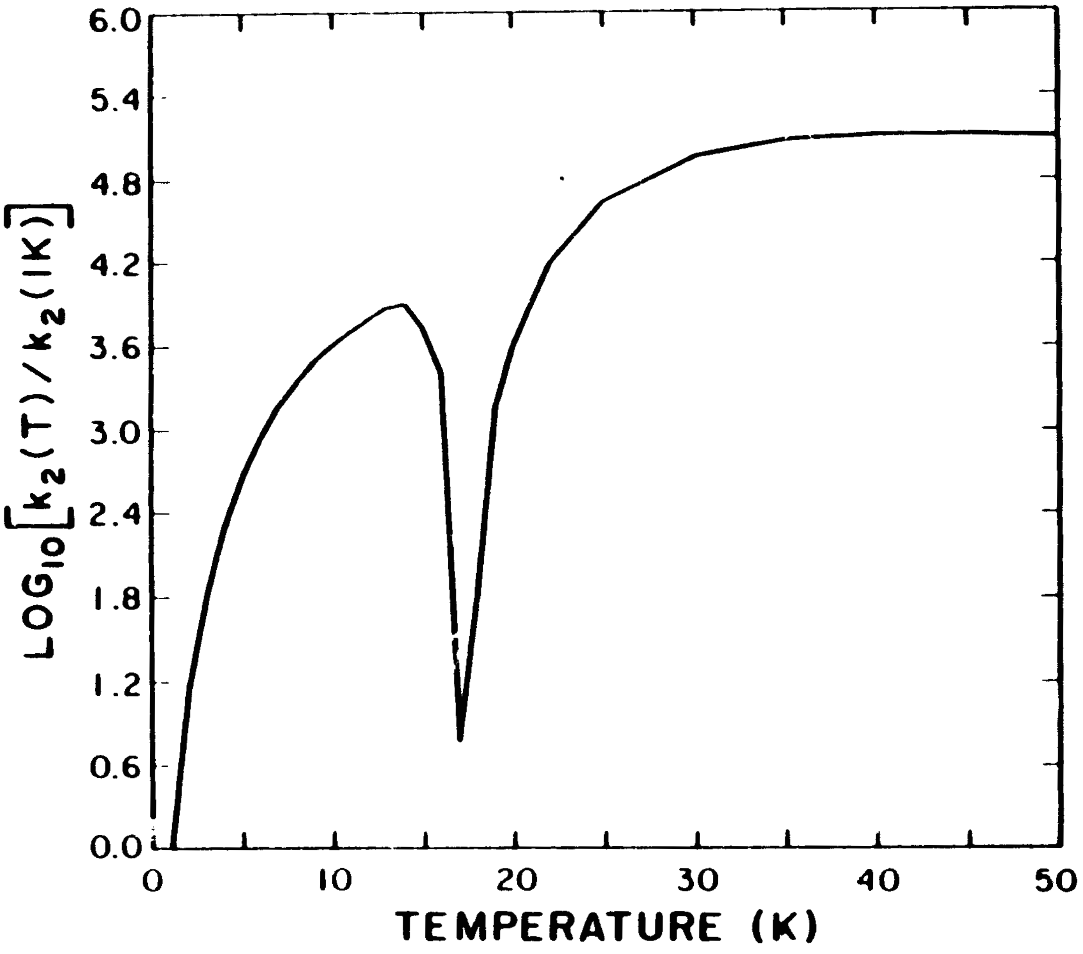
T(K)	k_2	T(K)	k_2	T(K)	k_2
1	.01164	20	47.87	135	17.58
2	.1644	22	181.1	140	31.42
3	.7736	25	510.3	150	62.62
4	2.324	30	1049	160	104.3
5	5.408	35	1365	170	147.2
6	10.38	40	1467	180	188.2
7	17.24	45	1467	190	223.6
8	26.13	50	1387	200	251.8
9	36.78	60	1141	210	288.4
10	48.48	70	555.7	220	319.6
11	60.17	80	507.9	230	344.0
12	72.17	90	266.4	240	364.0
13	87.42	100	113.7	250	378.4
14	94.11	105	65.46	260	398.0
15	62.08	110	33.83	270	414.6
16	30.64	115	12.29	280	429.3
17	.06894	120	1.883	290	438.0
18	.8661	125	.4296	300	448.1
19	16.99	130	6.347		

Figure 13. Thermoelastic attenuation for silicon along [111] direction from Eq. (3.13).



LOG$_{10}$[k$_2$(T)/k$_2$(1K)]
0.0
0.6
1.2
1.8
2.4
3.0
3.6
4.2
4.8
5.4
6.0
0
60
120
180
240
300
TEMPERATURE (K)

Figure 14. Thermoelastic attenuation for silicon along [111] direction from Eq. (3.13).


6.0
5.4
4.8
4.2
3.6
3.0
2.4
1.8
1.2
0.6
0.0
0
10
20
30
40
50
TEMPERATURE (K)
$\mathrm{LOG}_{10}\left[k_2(T)/k_2(1K)\right]$

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Chapter 4

Conclusions

> "And this is the record,
> that God hath given to us
> eternal life, and this life
> is in his Son. He that
> hath the Son hath life; and
> he that hath not the Son of
> God hath not life."
>
> I John 5:11,12

In this final chapter we summarize the main features of the work presented in the previous chapters and offer some suggestions for future research.

It has been found that long-range, nonlocal dipole-dipole interactions are able to provide lowering of the frequencies of the TA modes in diamond structure crystals. The dipoles also have the feature of not affecting the elastic constants or Raman frequency. It was necessary to include central potential interactions to fourth neighbors in order to fine tune the agreement with experiment. A reasonable fit to the experimental data has been obtained that exhibits a rapid fall off of the first and second order potential derivatives with increasing distance.

It is believed that further investigation of long-range electrostatic interactions in diamond structure crystals will be profitable. Specifically, one might examine the effect of including the local quadrupoles of Lax,[1] in addition to the nonlocal dipoles, in an effort to obtain agreement with experiment using a smaller number of parameters. The resulting dipole-quadrupole and quadrupole-quadrupole interactions should improve the problem of the angular variation of the dipolar interaction energy. In addition, one might also examine the effect of the short-range corrections to the dipole-dipole interaction energy as discussed in Appendix B. These short-range corrections have a different angular variation than the usual dipole-dipole interaction energy.

An anharmonic model has been developed that is a consistent extension of the harmonic model. Using this model we have obtained analytic expressions for the mode Grüneisen parameters that explain in a simple way the origin of the negative mode gammas. The relation of negative mode gammas to nearest neighbor central force instability is illustrated by these analytic expressions. It has been found that the approximation of neglecting first and second order potential derivatives in comparison with third order potential derivatives is particularly severe in the diamond structure. It has also been found that long-range anharmonicity is necessary to explain the experimental mode gammas in silicon and that the short-range anharmonicity calculations of Dolling and Cowley[2] and Jex[3] are inadequate to obtain even moderate agreement with experiment. Using the model developed in the present work, a reasonable fit to the experimental mode gammas for silicon has been obtained that exhibits a rapid fall off of the third order potential derivatives with increasing distance.

The volume thermal expansion coefficient of silicon has been calculated from 5K to 1700K using the above lattice dynamical model. Surprisingly good agreement with experiment from 17K to the melting point of 1687K has been obtained. This shows that higher order anharmonic contributions to the thermal expansion for silicon are very small, even at temperatures near the melting point. To further improve agreement with experiment below 17K , it is suggested that more than 60 special $\vec{k}$ points be used in evaluating the sum over the Brillouin zone. It is also believed that a better fit to the experimental mode gamma at the L point would improve agreement with experiment in the region of 75K , where the thermal expansion becomes the most negative.

Associated with the negative thermal expansion, it was found that silicon has an anomalous thermoelastic effect. It has been shown that this contribution to the acoustic attenuation exhibits strong attenuation anomalies in the vicinity of 17K and 125K . This investigation is preliminary in nature and demonstrates that anharmonic attenuation can vary rapidly in a narrow range of temperature. It is the present author's conviction that a calculation of the viscosity tensor for silicon as a function of temperature will exhibit anomalies as well. However, exsisting expressions[4] for the viscosity tensor of a solid can be objected to on fundamental grounds, and before a proper calculation can be made, a new theory of the viscosity tensor must be developed. The present author has investigated such a theory but since the results are not yet complete, they will not be reported on here.

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Appendix A

ANGLE BENDING CONTRIBUTION TO THE POTENTIAL ENERGY

In this appendix we derive an expression for the change in angle between any three atoms in a crystal correct to first order in the atomic displacements. The discussion is similar to that given by Trullinger[1] and is included here for the sake of completeness.

From the geometry of Fig. 5 and the definition of the dot product we have

$$\cos\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \frac{\vec{x}(\ell\kappa|\ell'\kappa')\cdot\vec{x}(\ell\kappa|\ell''\kappa'')}{|\vec{x}(\ell\kappa|\ell'\kappa')|\,|\vec{x}(\ell\kappa|\ell''\kappa'')|}\,, \qquad \text{(A-1)}$$

where

$$\vec{x}(\ell\kappa|\ell'\kappa') = \vec{x}(\ell\kappa) - \vec{x}(\ell'\kappa')\ , \qquad \text{(A-2)}$$

and

$$\vec{x}(\ell\kappa) = \vec{R}(\ell\kappa) + \vec{u}(\ell\kappa)\ . \qquad \text{(A-3)}$$

Now

$$\vec{x}(\ell\kappa|\ell'\kappa')\cdot\vec{x}(\ell\kappa|\ell''\kappa'') = \left[\begin{array}{l} \vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{R}(\ell\kappa|\ell''\kappa'') + \\ + \vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell''\kappa'') \\ + \vec{R}(\ell\kappa|\ell''\kappa'')\cdot\vec{u}(\ell\kappa|\ell'\kappa') + \\ + \vec{u}(\ell\kappa|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell''\kappa'') \end{array}\right]. \qquad \text{(A-4)}$$

where

$$\vec{R}(\ell\kappa|\ell'\kappa') = \vec{R}(\ell\kappa) - \vec{R}(\ell'\kappa') \,, \qquad \text{(A-5)}$$

and

$$\vec{u}(\ell\kappa|\ell'\kappa') = \vec{u}(\ell\kappa) - \vec{u}(\ell'\kappa') \,. \qquad \text{(A-6)}$$

We also have

$$|\vec{x}(\ell\kappa|\ell'\kappa')| = |\vec{R}(\ell\kappa|\ell'\kappa')| \left[1 + \frac{2\vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|^2} + \frac{|\vec{u}(\ell\kappa|\ell'\kappa')|^2}{|\vec{R}(\ell\kappa|\ell'\kappa')|^2} \right]^{\frac{1}{2}} . \qquad \text{(A-7)}$$

Using the expansion

$$(1+y)^{-1/2} = 1 - \frac{1}{2}\,y + \frac{3}{8}\,y^2 + \cdots \,, \qquad \text{(A-8)}$$

we have to first order in the displacements that

$$|\vec{x}(\ell\kappa|\ell'\kappa')|^{-1} = |\vec{R}(\ell\kappa|\ell'\kappa')|^{-1} \left[1 - \frac{\vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|^2} \right] . \qquad \text{(A-9)}$$

Combining Eqs. (A-1), (A-4) and (A-9) we obtain to first order in the displacements that

$$\cos\,\theta(\kappa|\ell'\kappa'|\ell''\kappa'') = \cos\,\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') -$$

$$- \cos\,\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\left[\frac{\vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|^2}\right]$$

$$- \cos\,\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\left[\frac{\vec{R}(\ell\kappa|\ell''\kappa'')\cdot\vec{u}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell''\kappa'')|^2}\right]$$

$$+ \frac{\vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|} + \frac{\vec{R}(\ell\kappa|\ell''\kappa'')\cdot\vec{u}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|}\ , \qquad \text{(A-10)}$$

where we have defined the equilibrium angles by

$$\cos\,\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \frac{\vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{R}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell''\kappa'')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|}\ . \qquad \text{(A-11)}$$

Defining the change in angle from the equilibrium angle by

$$\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') - \theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\ , \qquad \text{(A-12)}$$

we can use the fact that

$$\cos\,\theta = \cos(\theta^{(0)}+\Delta\theta) = \cos\,\theta^{(0)}\cos\,\Delta\theta - \sin\,\theta^{(0)}\sin\,\Delta\theta\ , \qquad \text{(A-13)}$$

so that to first order in $\Delta\theta$

$$\cos(\theta^{(0)} + \Delta\theta) = \cos\,\theta^{(0)} - \Delta\theta\,\sin\,\theta^{(0)}\ , \qquad \text{(A-14)}$$

or

$$\Delta\theta = \left(\cot\theta^{(0)} - \frac{\cos\theta}{\sin\theta^{(0)}}\right) . \qquad \text{(A-15)}$$

Using Eq. (A-15) together with Eq. (A-10) we obtain

$$\begin{aligned}
&\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \\
&= \cot\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\left[\frac{\vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|^2}\right] \\
&+ \cot\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\left[\frac{\vec{R}(\ell\kappa|\ell''\kappa'')\cdot\vec{u}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell''\kappa'')|^2}\right] \\
&- \csc\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\left[\frac{\vec{R}(\ell\kappa|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|}\right] \\
&- \csc\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\left[\frac{\vec{R}(\ell\kappa|\ell''\kappa'')\cdot\vec{u}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|}\right].
\end{aligned}$$

(A-16)

Defining

$$\begin{aligned}
&\vec{\eta}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \\
&= \cot\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\left[\frac{\vec{R}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|^2}\right] \\
&- \csc\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\left[\frac{\vec{R}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|}\right] ,
\end{aligned}$$

(A-17)

Eq. (A-16) can be rewritten as

$$\begin{aligned}
\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = {} & \vec{\eta}(\ell\kappa|\ell'\kappa'|\ell''\kappa')\cdot\vec{u}(\ell\kappa|\ell'\kappa') \\
& + \vec{\eta}(\ell\kappa|\ell''\kappa''|\ell'\kappa')\cdot\vec{u}(\ell\kappa|\ell''\kappa''), \qquad \text{(A-18)}
\end{aligned}$$

or in component form

$$\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \sum_{\alpha} \eta_{\alpha}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')u_{\alpha}(\ell\kappa|\ell'\kappa')$$

$$+ \sum_{\alpha} \eta_{\alpha}(\ell\kappa|\ell''\kappa''|\ell'\kappa')u_{\alpha}(\ell\kappa|\ell''\kappa'') \ . \qquad \text{(A-19)}$$

Note that Eq. (A-18) depends explicitly on differences of displacements so that it satisfies infinitesimal translation invariance. Using Eq. (A-18) it is easy to show infinitesimal rotation invariance. Consider the infinitesimal rotation

$$\vec{u}(\ell\kappa) = \vec{\omega}\times(\vec{R}(\ell\kappa)-\vec{R}_o) \ , \qquad \text{(A-20)}$$

where $|\vec{\omega}|$ is the infinitesimal rotation angle and $\vec{R}_o$ is the origin of the rotation. Then we have

$$\vec{u}(\ell\kappa|\ell'\kappa') = \vec{\omega}\times\vec{R}(\ell\kappa|\ell'\kappa') \ . \qquad \text{(A-21)}$$

Substituting Eq. (A-21) into Eq. (A-18) and using the vector identity that

$$\vec{A}\cdot(\vec{B}\times\vec{C}) = -\vec{B}\cdot(\vec{A}\times\vec{C}) \ , \qquad \text{(A-22)}$$

we obtain

$$\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = -\vec{\omega}\cdot\left[\begin{array}{l}\vec{\eta}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\times\vec{R}(\ell\kappa|\ell'\kappa') \\ +\vec{\eta}(\ell\kappa|\ell''\kappa''|\ell'\kappa')\times\vec{R}(\ell\kappa|\ell''\kappa'')\end{array}\right] . \tag{A-23}$$

From Eq. (A-17) we see that

$$\vec{\eta}(\ell\kappa|\ell'\kappa'|\ell''\kappa'') \times \vec{R}(\ell\kappa|\ell'\kappa') = - \csc\,\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\,\frac{\vec{R}(\ell\kappa|\ell''\kappa'')\times\vec{R}(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|} , \tag{A-24}$$

and similarly

$$\vec{\eta}(\ell\kappa|\ell''\kappa''|\ell'\kappa') \times \vec{R}(\ell\kappa|\ell''\kappa'') = - \csc\,\theta^{(0)}(\ell\kappa|\ell'\kappa'|\ell''\kappa'')\,\frac{\vec{R}(\ell\kappa|\ell'\kappa')\times\vec{R}(\ell\kappa|\ell''\kappa'')}{|\vec{R}(\ell\kappa|\ell'\kappa')|\,|\vec{R}(\ell\kappa|\ell''\kappa'')|} . \tag{A-25}$$

In obtaining Eq. (A-25) we have made use of the property that

$$\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = \theta(\ell\kappa|\ell''\kappa''|\ell'\kappa') . \tag{A-26}$$

Adding Eqs. (A-24) and (A-25) we obtain

$$\Delta\theta(\ell\kappa|\ell'\kappa'|\ell''\kappa'') = 0 , \tag{A-27}$$

under the infinitesimal rotation Eq. (A-20). Thus the change in angle Eq. (A-18) satisfies infinitesimal rotation invariance.

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Appendix B

ELECTROSTATIC INTERACTION ENERGIES IN A NONLOCAL DIELECTRIC MEDIUM.

In this appendix we discuss the interaction energy of two charge distributions in a particular type of linear, nonlocal dielectric medium. Results for the interaction energies of the first few cartesian multipoles are presented. Further application to the case of isotropic nonlocality is made. The special case appropriate to semiconductors is examined.

Consider the interaction energy of two charge distributions in a linear dielectric medium. We have[1]

$$W_{12} = \frac{1}{8\pi}\int d^3x(\vec{E}_1\cdot\vec{D}_2+\vec{E}_2\cdot\vec{D}_1) \ , \qquad \text{(B-1)}$$

where

$$\nabla\cdot\vec{D}_1 = 4\pi\rho_1 \qquad \nabla\cdot\vec{D}_2 = 4\pi\rho_2 \ , \qquad \text{(B-2a)}$$

$$\vec{D} = \vec{D}_1+\vec{D}_2 \qquad \vec{E} = \vec{E}_1+\vec{E}_2 \ . \qquad \text{(B-2b)}$$

Introducing the Fourier transforms

$$f(\vec{x}) = \int d^3x \ e^{i\vec{k}\cdot\vec{x}} f(\vec{k}) \qquad \text{(B-3a)}$$

$$f(\vec{k}) = \frac{1}{(2\pi)^3}\int d^3x \ e^{-i\vec{k}\cdot\vec{x}} f(\vec{x}) \ , \qquad \text{(B-3b)}$$

we suppose for the medium of interest that

$$\vec{D}(\vec{k}) = \epsilon(\vec{k})\vec{E}(\vec{k}) \ . \qquad \text{(B-3b)}$$

This corresponds to examining the diagonal part of the dielectric matrix, or neglect of umklapp terms for a crystal.[2] These terms have been shown to be small for silicon and germanium as anticipated by Penn.[3] After some algebra and use of Eqs. (B1-B4) we obtain

$$W_{12} = \frac{1}{8\pi}\int d^3x \int d^3x' g(\vec{x}-\vec{x}')\rho_1(\vec{x})\rho_2(\vec{x}') \ , \qquad \text{(B-5a)}$$

with

$$g(x) = \frac{1}{(2\pi)^2} \int d^3k \ \frac{(e^{i\vec{k}\cdot\vec{x}}+e^{-i\vec{k}\cdot\vec{x}})}{k^2\epsilon(\vec{k})} \ . \qquad \text{(B-5b)}$$

Note also that

$$g(\vec{x}) = g(-\vec{x}) \ . \qquad \text{(B-5c)}$$

All the nonlocal behaviour resides in the function $g(\vec{x})$.

Now consider the first few terms of a cartesian multipole expansion about the point $\vec{x}'$. We have

$$\rho(\vec{x}) = Q\delta(\vec{x}-\vec{x}') - \sum_{\alpha} p_{\alpha} \frac{\partial}{\partial x_{\alpha}} \delta(\vec{x}-\vec{x}')$$

$$+ \frac{1}{2} \sum_{\alpha,\beta} Q_{\alpha\beta} \frac{\partial^2}{\partial x_{\alpha}\partial x_{\beta}} \delta(\vec{x}-\vec{x}')$$

$$+ \text{(higher multipoles)} \ , \qquad \text{(B-6)}$$

where $\delta(\vec{x})$ is the Dirac delta function. Direct integration of Eq. (B-6) gives

$$Q = \int_{V'} d^3x \rho(\vec{x}) \tag{B-7a}$$

$$p_\alpha = \int_{V'} d^3x \, x_\alpha \rho(\vec{x}) \tag{B-7b}$$

$$Q_{\alpha\beta} = \int_{V'} d^3x \, x_\alpha x_\beta \rho(\vec{x}) \ , \tag{B-7c}$$

where V' is the volume to which the charge density is localized. Eq. (B-6) can be obtained by application of Poisson's equation to determine the charge densities responsible for monopole, dipole and quadrupole potentials. Utilizing Eq. (B-6) in Eq. (B-5a) we obtain

$$\begin{aligned} W_{12} = \int d^3x \int d^3x' g(\vec{x}-\vec{x}\,')[Q_1 \delta(\vec{x}-\vec{x}_1) - \sum_\alpha p_\alpha(1) \frac{\partial}{\partial x_\alpha} \delta(\vec{x}-\vec{x}_1) \\ + \frac{1}{2} \sum_{\alpha,\beta} Q_{\alpha\beta}(1) \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \delta(\vec{x}-\vec{x}_1)] \times [Q_2 \delta(\vec{x}\,'-\vec{x}_2) \\ - \sum_\mu p_\mu(2) \frac{\partial}{\partial x'_\mu} \delta(\vec{x}\,'-\vec{x}_2) + \frac{1}{2} \sum_{\mu,\nu} Q_{\mu\nu}(2) \frac{\partial^2}{\partial x'_\mu \partial x'_\nu} \delta(\vec{x}\,'-\vec{x}_2)] \ . \end{aligned} \tag{B-8}$$

Multiplying out the various terms yields

$$\begin{aligned} W_{12} = W_{12}^{MM} + W_{12}^{Md} + W_{12}^{MQ} + W_{12}^{dd} + W_{12}^{dQ} + W_{12}^{QQ} \\ + \text{(higher multipoles)} \ , \end{aligned} \tag{B-9}$$

where

$$W_{12}^{MM} = \int d^3x \int d^3x' g(\vec{x}-\vec{x}')Q_1Q_2\delta(\vec{x}-\vec{x}_1)\delta(\vec{x}'-\vec{x}_2) \tag{B-10a}$$

$$\begin{aligned} W_{12}^{Md} = -\int d^3x \int d^3x' g(\vec{x}-\vec{x}')[Q_1\delta(\vec{x}-\vec{x}_1)\sum_{\alpha} p_{\alpha}(2)\frac{\partial}{\partial x'_{\alpha}}\delta(\vec{x}'-\vec{x}_2) \\ + Q_2\delta(\vec{x}'-\vec{x}_2)\sum_{\alpha} p_{\alpha}(1)\frac{\partial}{\partial x_{\alpha}}\delta(\vec{x}-\vec{x}_1)] \end{aligned} \tag{B-10b}$$

$$\begin{aligned} W_{12}^{MQ} = \frac{1}{2}\int d^3x \int d^3x' g(\vec{x}-\vec{x}')[Q_1\delta(\vec{x}-\vec{x}_1)\sum_{\alpha,\beta} Q_{\alpha\beta}(2)\frac{\partial^2}{\partial x'_{\alpha}\partial x'_{\beta}}\delta(\vec{x}'-\vec{x}_2) \\ + Q_2\delta(\vec{x}'-\vec{x}_2)\sum_{\alpha,\beta} Q_{\alpha\beta}(1)\frac{\partial^2}{\partial x_{\alpha}\partial x_{\beta}}\delta(\vec{x}-\vec{x}_1)] \end{aligned} \tag{B-10c}$$

$$\begin{aligned} W_{12}^{dd} = \sum_{\alpha,\beta}\int d^3x \int d^3x' g(\vec{x}-\vec{x}')p_{\alpha}(1)p_{\beta}(2)\left[\frac{\partial\delta(\vec{x}-\vec{x}_1)}{\partial x_{\alpha}} \times\right. \\ \left.\times \frac{\partial\delta(\vec{x}'-\vec{x}_2)}{\partial x'_{\beta}}\right] \quad . \end{aligned} \tag{B-10d}$$

$$\begin{aligned} W_{12}^{dQ} = -\frac{1}{2}\sum_{\alpha,\mu,\nu}\int d^3x \int d^3x' g(\vec{x}-\vec{x})\left[p_{\alpha}(1)\frac{\partial\delta(\vec{x}-\vec{x}_1)}{\partial x_{\alpha}} \times\right. \\ \times Q_{\mu\nu}(2)\frac{\partial^2\delta(\vec{x}'-\vec{x}_2)}{\partial x'_{\mu}\partial x'_{\nu}} + p_{\alpha}(2)\frac{\partial\delta(\vec{x}'-\vec{x}_2)}{\partial x'_{\alpha}} \times \\ \left.\times Q_{\mu\nu}(1)\frac{\partial^2\delta(\vec{x}-\vec{x}_1)}{\partial x_{\mu}\partial x_{\nu}}\right] \end{aligned} \tag{B-10e}$$

$$\begin{aligned} W_{12}^{QQ} = \frac{1}{4}\sum_{\alpha\beta\mu\nu} Q_{\alpha\beta}(1)Q_{\mu\nu}(2)\int d^3x \int d^3x' g(\vec{x}-\vec{x}') \times \\ \times \left[\left(\frac{\partial^2\delta(\vec{x}-\vec{x}_1)}{\partial x_{\alpha}\partial x_{\beta}}\right)\left(\frac{\partial^2\delta(\vec{x}'-\vec{x}_2)}{\partial x_{\mu}\partial x_{\nu}}\right)\right] \quad . \end{aligned} \tag{B-10f}$$

The terms in Eqs. (B-9) and (B-10) correspond to monopole-monopole interaction, monopole-dipole, monopole-quadrupole, dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively. We now proceed to evaluate the various integrals in Eqs. (B-10).

For the monopole-monopole term Eq. (B-10a) yields immediately

$$W_{12}^{MM} = Q_1 Q_2 g(\vec{x}_1 - \vec{x}_2) \ . \tag{B-11}$$

Thus we see that $g(\vec{x})$ is essentially the modified Coulomb's law for the nonlocal medium.

Consider next the monopole-dipole term. We can immediately perform one integration, the remaining integration to be done by parts so that Eq. (B-10b) becomes

$$W_{12}^{Md} = \sum_{\alpha} \left[Q_1 p_{\alpha}(2) \frac{\partial g(\vec{x}_1 - \vec{x}_2)}{\partial x_{2\alpha}} + Q_2 p_{\alpha}(1) \frac{\partial g(\vec{x}_1 - \vec{x}_2)}{\partial x_{1\alpha}} \right] \ . \tag{B-12}$$

Two partial integrations give for the monopole-quadrupole term

$$W_{12}^{MQ} = \frac{1}{2} \sum_{\alpha,\beta} \left[Q_1 Q_{\alpha\beta}(2) \frac{\partial^2 g(\vec{x}_1 - \vec{x}_2)}{\partial x_{2\alpha} \partial x_{2\beta}} + Q_2 Q_{\alpha\beta}(1) \frac{\partial^2 g(x_1 - x_2)}{\partial x_{1\alpha} \partial x_{1\beta}} \right] , \tag{B-13}$$

and for the dipole-dipole term

$$W_{12}^{dd} = \sum_{\alpha,\beta}\left[\frac{\partial^2}{\partial x_{1\alpha}\partial x_{2\beta}}\, g(\vec{x}_1-\vec{x}_2)\right] p_\alpha(1)p_\beta(2) \ . \qquad \text{(B-14)}$$

Three integrations by parts give for the dipole-quadrupole term

$$W_{12}^{dQ} = \frac{1}{2}\sum_{\alpha,\mu,\nu}\left[p_\alpha(1)Q_{\mu\nu}(2)\frac{\partial^3 g(\vec{x}_1-\vec{x}_2)}{\partial x_{1\alpha}\partial x_{2\mu}\partial x_{2\nu}} + p_\alpha(2)Q_{\mu\nu}(1)\frac{\partial^3 g(\vec{x}_1-\vec{x}_2)}{\partial x_{2\alpha}\partial x_{1\mu}\partial x_{2\nu}}\right] \ . \qquad \text{(B-15)}$$

Finally, the quadrupole-quadrupole term is obtained by four partial integrations yielding

$$W_{12}^{QQ} = \frac{1}{4}\sum_{\substack{\alpha\beta\\ \mu\nu}}\left[\frac{\partial^4 g(\vec{x}_1-\vec{x}_2)}{\partial x_{1\alpha}\partial x_{1\beta}\partial x_{2\mu}\partial x_{2\nu}}\right] Q_{\alpha\beta}(1)Q_{\mu\nu}(2) \ . \qquad \text{(B-16)}$$

Having obtained these general results, we now examine the case when

$$\epsilon(\vec{k}) = \epsilon(k) \quad \text{where} \quad k = |\vec{k}| \ . \qquad \text{(B-17)}$$

Using the definition Eq. (B-5b) and integrating over angles we obtain

$$g(\vec{x}) = \frac{f(|\vec{x}|)}{|\vec{x}|} \ , \qquad \text{(B-18a)}$$

where

$$f(r) = \frac{2}{\pi}\int_0^\infty dk\, \frac{\sin kr}{k\epsilon(k)} . \tag{B-18b}$$

Using the form of Eq. (B-18a) and differentiating gives

$$\begin{aligned}\frac{\partial^2 g(\vec{x}_1-\vec{x}_2)}{\partial x_{1\alpha}\partial x_{2\beta}} = \Bigg[&\Omega_{\alpha\beta}(1|2) f(|\vec{x}_1-\vec{x}_2|) \\ &- \Omega_{\alpha\beta}(1|2)\,|\vec{x}_1-\vec{x}_2|\, f'(|\vec{x}_1-\vec{x}_2|) \\ &- \frac{(x_{1\alpha}-x_{2\alpha})(x_{1\beta}-x_{2\beta})}{|\vec{x}_1-\vec{x}_2|^3}\, f''(|\vec{x}_1-\vec{x}_2|)\Bigg] ,\end{aligned} \tag{B-19a}$$

with

$$\Omega_{\alpha\beta}(1|2) = \left[\frac{\delta_{\alpha\beta}}{|\vec{x}_1-\vec{x}_2|^3} - \frac{3(x_{1\alpha}-x_{2\alpha})(x_{1\beta}-x_{2\beta})}{|\vec{x}_1-\vec{x}_2|^5}\right], \tag{B-19b}$$

$$f'(|\vec{x}_1-\vec{x}_2|) = \left.\frac{d^2 f(r)}{dr}\right|_{r=|\vec{x}_1-\vec{x}_2|} , \tag{B-19c}$$

$$f''(|\vec{x}_1-\vec{x}_2|) = \left.\frac{d^2 f(r)}{dr^2}\right|_{r=|\vec{x}_1-\vec{x}_2|} . \tag{B-19d}$$

Defining

$$J_{\alpha\beta}(1|2) = \frac{\partial^2 g(\vec{x}_1-\vec{x}_2)}{\partial x_{1\alpha}\partial x_{2\beta}} , \tag{B-20}$$

the dipole-dipole interaction Eq. (B-14) can be written as

$$W_{12}^{dd} = \sum_{\alpha,\beta} J_{\alpha\beta}(1|2)p_{\alpha}(1)p_{\beta}(2) \quad . \tag{B-21}$$

Eq. (B-19a) is the dipole-dipole interaction law in the nonlocal medium. Note that it contains terms in addition to the usual free space term, which is obtained by setting f equal to one. The extra terms are a consequence of the nonlocal nature of the medium.

Now we want to examine a special form for $\epsilon(\vec{k})$ appropriate to a semiconductor. Walter and Cohen[4] have shown that the effects of anisotropy are very small for several semiconductors, thus justifying the use of an isotropic form for $\epsilon(\vec{k})$. For this case, one can define a spatial dielectric function $\tilde{\epsilon}(r)$ by the relation

$$v(r) = \frac{Ze}{\tilde{\epsilon}(r)r} \quad , \tag{B-22}$$

where $v(r)$ is the screened Coulomb potential of a point charge Ze . In fact, one can show that

$$f(r) = \frac{1}{\tilde{\epsilon}(r)} \quad , \tag{B-23}$$

with $f(r)$ given by Eq. (B-18b).

Using the Penn model,[5] Srinivasan[6] has shown for silicon that $\tilde{\epsilon}(r)$ essentially reaches its value at infinity by the nearest-neighbor distance. This somewhat surprising conclusion can be made plausible as follows. With four valence electrons per atom and two atoms per primitive cell, the valence electron concentration of the diamond structure is

$$n_V = \frac{8}{\Omega_o} = \frac{32}{a^3} , \tag{B-24}$$

so that the Fermi wavenumber is

$$k_F = (3\pi^2 n_V)^{1/3} = \frac{2\pi}{a}\left(\frac{12}{\pi}\right)^{1/3} , \tag{B-25a}$$

or

$$k_F = (1.5631853)\frac{2\pi}{a} . \tag{B-25b}$$

For silicon one finds

$$\frac{1}{k_F} = 0.5529 \text{ Å} , \tag{B-26}$$

which is rather short indeed. One expects screening on this length scale.

To be more quantitative, the results of Walter and Cohen[7] can be fit rather closely by the functional form

$$\epsilon(k) = \left[1 + \frac{(\epsilon-1)\mu^2}{k^2+\mu^2}\right], \tag{B-27}$$

where ϵ is the static, bulk dielectric constant. The measured value of ϵ is 11.7 for silicon.[8] Using Eq. (B-27) and performing the integral in Eq. (B-18b) yields

$$f(r) = \left[\frac{1}{\epsilon} + \left(1 - \frac{1}{\epsilon}\right)e^{-\sqrt{\epsilon}\,\mu r}\right] . \tag{B-28}$$

From the work of Walter and Cohen we find for silicon that

$$\mu = \lambda\left(\frac{2\pi}{a}\right) \quad \text{with} \quad \lambda = 0.45 \ , \tag{B-29}$$

so that

$$\mu\sqrt{\epsilon} = (1.54)\frac{2\pi}{a} \ , \tag{B-30}$$

or a screening length of

$$\frac{1}{\mu\sqrt{\epsilon}} = 0.56\ \text{Å} \ . \tag{B-31}$$

Note the close agreement of Eqs. (B-26) and (B-31). Differentiation of Eq. (B-28) gives

$$f'(r) = -\sqrt{\epsilon}\ \mu\left(1 - \frac{1}{\epsilon}\right)e^{-\sqrt{\epsilon}\,\mu r} \ , \tag{B-32a}$$

$$f''(r) = \epsilon\mu^2\left(1 - \frac{1}{\epsilon}\right)e^{-\sqrt{\epsilon}\,\mu r} \ . \tag{B-32b}$$

In Table B1 f and its first two derivatives are evaluated for silicon at the distances of the first few neighbors. As can be seen from the Table, f is within one percent of its value at infinity by the second neighbor distance.

From Eq. (B-19a) we see that the first derivative term has the same angular variation as the term with no derivative. However, the term with the second derivative has a different angular variation than the other two terms. This could give a sizeable contribution to the dipole-dipole interaction energy out to about third nearest neighbors. Thus we see that we can write the dipole-dipole interaction in the form

$$W_{12}^{dd} = \frac{1}{\epsilon} \sum_{\alpha,\beta} \Omega_{\alpha\beta}(1|2) p_\alpha(1) p_\beta(2) \tag{B-33}$$

$$+ \text{(exponential terms)} ,$$

where the exponential terms are very short ranged.

TABLE B1

Eqs. (B-28) and (B-32) evaluated for the first few neighbors of silicon.

r	$f(r)$	$rf'(r)$	$r^2f'(r)$
r_0	9.932×10^{-2}	-5.804×10^{-2}	2.432×10^{-1}
r_2	8.645×10^{-2}	-6.682×10^{-3}	4.572×10^{-2}
r_3	8.577×10^{-2}	-2.405×10^{-3}	1.930×10^{-2}
r_4	8.553×10^{-2}	-5.554×10^{-4}	5.374×10^{-3}
∞	8.547×10^{-2}	0	0

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Appendix C

QUADRUPOLE MOMENT DUE TO AN ARRAY OF DIPOLES

We begin with the charge density $\rho(\vec{x})$ due to an array of dipoles $\vec{p}(\ell\kappa)$ located at sites $\vec{R}(\ell\kappa)$.

$$\rho(\vec{x}) = -\sum_{\ell\kappa} \vec{p}(\ell\kappa)\cdot\nabla\delta(\vec{x}-\vec{R}(\ell\kappa)) \ . \tag{C-1}$$

Defining the total quadrupole moment as

$$Q_{\alpha\beta} = \int d^3x \ x_\alpha x_\beta \rho(\vec{x}) \ , \tag{C-2}$$

we find after integration by parts that for the array of dipoles

$$Q_{\alpha\beta} = \sum_{\ell\kappa}\left[R_\alpha(\ell\kappa)p_\beta(\ell\kappa)+R_\beta(\ell\kappa)p_\alpha(\ell\kappa)\right] \ . \tag{C-3}$$

Now consider the special case of the Raman mode in the diamond structure. For this mode $u_\alpha(\ell,0) = -u_\alpha(\ell,1) = u_\alpha$. Using Eqs. (1.149) and (1.151a) we find that

$$p_\alpha(\ell,0) = -\ 8p_1u_\alpha \tag{C-4a}$$

$$p_\alpha(\ell,1) = +\ 8p_1u_\alpha \ . \tag{C-4b}$$

Clearly there is no total dipole moment due to this mode, since the dipole moments in each unit cell are equal and opposite and thus add to zero. Using Eq. (C-3) and the position vectors Eq. (1.1) we have

$$Q_{\alpha\beta} = 8p_1 \sum_{\ell} \left[R_\alpha(1)u_\beta + R_\beta(1)u_\alpha \right] . \qquad \text{(C-5)}$$

Performing the sum on ℓ and using Eq. (1.5) we obtain

$$\begin{aligned} Q_{\alpha\beta} = 2ap_1N \Big[& (\delta_{\alpha 1}+\delta_{\alpha 2}+\delta_{\alpha 3})u_\beta + \\ & + (\delta_{\beta 1}+\delta_{\beta 2}+\delta_{\beta 3})u_\alpha \Big] \quad , \end{aligned} \qquad \text{(C-6)}$$

where N is the number of unit cells of the crystal. Thus we see that the Raman mode has a macroscopic quadrupole moment associated with it, where by macroscopic we mean proportional to the number of unit cells. Note also that only the p_1 term of Eq. (1.150) contributes to the quadrupole moment of this mode.

Appendix D

THE EWALD METHOD AND ITS APPLICATION TO DIPOLE SUMS.

In this appendix we discuss the Ewald method for transforming lattice sums to rapidly convergent form. The method is applied to dipole sums in the diamond structure.

We want to evaluate the sums Eqs. (1.168)

$$Q^{(1)}_{\alpha\beta}(\vec{k}) = \frac{\Omega_o}{4\pi} \sum_{\ell}{}' \Omega_{\alpha\beta}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \tag{D-1}$$

and

$$Q^{(2)}_{\alpha\beta}(\vec{k}) = \frac{\Omega_o}{4\pi} \sum_{\ell} \Omega_{\alpha\beta}(\ell,0|0,1)e^{-i\vec{k}\cdot\vec{R}(\ell)} \tag{D-2}$$

with

$$\Omega_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \left[\frac{\delta_{\alpha\beta}}{|\vec{R}(\ell\kappa|\ell'\kappa')|^3} - \frac{3R_\alpha(\ell\kappa|\ell'\kappa')R_\beta(\ell\kappa|\ell'\kappa')}{|\vec{R}(\ell\kappa|\ell'\kappa')|^5}\right] . \tag{D-3}$$

First we define

$$A_{\alpha\beta}(\vec{k},\vec{x}) = -\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\left[\sum_{\ell} \frac{e^{i\vec{k}\cdot\vec{R}(\ell)}}{|\vec{R}(\ell)-\vec{x}|}\right] . \tag{D-4}$$

Differentiating we obtain

$$A_{\alpha\beta}(\vec{k},\vec{x}) = \sum_{\ell}\left[\frac{\delta_{\alpha\beta}}{|\vec{R}(\ell)-\vec{x}|^3} - \frac{3(R_\alpha(\ell)-x_\alpha)(R_\beta(\ell)-x_\beta)}{|\vec{R}(\ell)-\vec{x}|^5}\right]e^{i\vec{k}\cdot\vec{R}(\ell)} . \tag{D-5}$$

Now

$$\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\frac{1}{|\vec{x}|} = -\left[\frac{\delta_{\alpha\beta}}{|\vec{x}|^3} - \frac{3x_\alpha x_\beta}{|\vec{x}|^5}\right] , \tag{D-6}$$

so that

$$\left[A_{\alpha\beta}(\vec{k},\vec{x}) + \frac{\partial^2}{\partial x_\alpha \partial x_\beta}\frac{1}{|\vec{x}|}\right] =$$

$$\sum_{\ell}{}' \left[\frac{\delta_{\alpha\beta}}{|\vec{R}(\ell)-\vec{x}|^3} - \frac{3(R_\alpha(\ell)-x_\alpha)(R_\beta(\ell)-x_\beta)}{|\vec{R}(\ell)-\vec{x}|^5}\right]e^{i\vec{k}\cdot\vec{R}(\ell)} , \tag{D-7}$$

where the prime on the sum indicates omit the $\ell = 0$ term. Thus we have

$$\lim_{\vec{x}\to 0}\left[A_{\alpha\beta}(-\vec{k},\vec{x}) + \frac{\partial^2}{\partial x_\alpha \partial x_\beta}\frac{1}{|\vec{x}|}\right] = \sum_{\ell}{}' \Omega_{\alpha\beta}(\ell,0|0,0)e^{-i\vec{k}\cdot\vec{R}(\ell)} \tag{D-8}$$

so that

$$Q^{(1)}_{\alpha\beta}(\vec{k}) = \frac{\Omega_o}{4\pi}\lim_{\vec{x}\to 0}\left[A_{\alpha\beta}(-\vec{k},\vec{x}) + \frac{\partial^2}{\partial x_\alpha \partial x_\beta}\frac{1}{|\vec{x}|}\right] . \tag{D-9}$$

Similarly from Eqs. (D-2) and (D-5) we have

$$A_{\alpha\beta}(-\vec{k},\vec{R}(1)) = \sum_{\ell}\Omega_{\alpha\beta}(\ell,0|0,1)e^{-i\vec{k}\cdot\vec{R}(\ell)} \tag{D-10}$$

so that

$$Q^{(2)}_{\alpha\beta}(\vec{k}) = \frac{\Omega_o}{4\pi} A_{\alpha\beta}(-\vec{k},\vec{R}(1)) \ . \tag{D-11}$$

From Eqs. (D-9) and (D-11) we see that it is sufficient to find an expression for $A_{\alpha\beta}(\vec{k},\vec{x})$. Next consider the sum

$$H(\vec{k},\vec{x}) = \sum_{\ell} \frac{e^{i\vec{k}\cdot\vec{R}(\ell)}}{|\vec{R}(\ell)-\vec{x}|} \tag{D-12}$$

using the integral representation

$$\frac{1}{|\vec{R}(\ell)-\vec{x}|} = \frac{2}{\sqrt{\pi}} \int_0^{\infty} d\rho \ e^{-\rho^2|\vec{R}(\ell)-\vec{x}|^2} \tag{D-13}$$

we have

$$H(\vec{k},\vec{x}) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} d\rho \left[\sum_{\ell} e^{-\rho^2|\vec{R}(\ell)-\vec{x}|^2} e^{i\vec{k}\cdot\vec{R}(\ell)}\right] \tag{D-14a}$$

or

$$H(\vec{k},\vec{x}) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} d\rho \ e^{i\vec{k}\cdot\vec{x}} \left[\sum_{\ell} e^{-\rho^2|\vec{R}(\ell)-\vec{x}|^2} e^{i\vec{k}\cdot(\vec{R}(\ell)-\vec{x})}\right] . \tag{D-14b}$$

Defining

$$F(\vec{x}) = \sum_{\ell} e^{-\rho^2|\vec{R}(\ell)-\vec{x}|^2} e^{i\vec{k}\cdot(\vec{R}(\ell)-\vec{x})} \tag{D-15}$$

we note that $F(\vec{x}) = F(\vec{x}+\vec{R}(m))$ where $\vec{R}(m)$ is a lattice translation vector. Thus $F(\vec{x})$ is periodic with the periodicity of the direct lattice and we can expand it in a fourier series[1]

$$F(\vec{x}) = \sum_{\vec{G}} F_{\vec{G}}\, e^{i\vec{G}\cdot\vec{x}} , \tag{D-16a}$$

with Fourier coefficients

$$F_{\vec{G}} = \frac{1}{\Omega_o} \int_{\Omega_o} d^3x\; F(\vec{x}) e^{-i\vec{G}\cdot\vec{x}} . \tag{D-16b}$$

The sum in Eq. (D-16a) is over all reciprocal lattice vectors and the integral in Eq. (E-16b) is over the primitive unit cell.

Substituting Eq. (D-15) into Eq. (D-16b) we have

$$F_{\vec{G}} = \frac{1}{\Omega_o} \sum_{\ell} \int_{\Omega_o} d^3x\; e^{-i\vec{G}\cdot\vec{x}} e^{-\rho^2|\vec{R}(\ell)-\vec{x}|^2} e^{i\vec{k}\cdot(\vec{R}(\ell)-\vec{x})} \tag{D-17}$$

letting

$$\vec{y} = \vec{x} - \vec{R}(\ell) \tag{D-18}$$

Eq. (D-17) becomes

$$F_{\vec{G}} = \frac{1}{\Omega_o} \sum_{\ell} \int_{\Omega_{-\ell}} d^3y\; e^{-\rho^2 y^2} e^{-i\vec{G}\cdot(\vec{R}(\ell)+\vec{y})} e^{-i\vec{k}\cdot\vec{y}} \tag{D-19}$$

where the integral is over the volume of the unit cell at the position $-\vec{R}(\ell)$. Since $e^{i\vec{G}\cdot\vec{R}(\ell)} = 1$ we have an identical integral for each unit cell so that

$$F_{\vec{G}} = \frac{1}{\Omega_o}\int_V d^3y\; e^{-\rho^2 y^2} e^{-i(\vec{k}+\vec{G})\cdot\vec{y}} \tag{D-20}$$

where the integral is now over the volume of the entire crystal. We now pass to the limit of a very large crystal so that the integral in Eq. (D-20) can be taken over all space. Evaluating the integral in Eq. (D-20) in rectangular coordinates we obtain

$$F_{\vec{G}} = \frac{\pi^{3/2}}{\Omega_o \rho^3}\, e^{-|\vec{k}+\vec{G}|^2/4\rho^2}\ , \tag{D-21}$$

so that Eq. (D-15) may be written as

$$F(\vec{x}) = \frac{\pi^{3/2}}{\Omega_o \rho^3}\sum_{\vec{G}} e^{-|\vec{k}+\vec{G}|^2/4\rho^2} e^{i\vec{G}\cdot\vec{x}}\ . \tag{D-22}$$

Returning to Eq. (D-14b) we break the integral into two parts and substitute the Fourier series Eq. (D-22) into the first integral to obtain

$$H(\vec{k},\vec{x}) = \frac{2\pi}{\Omega_o}\sum_{\vec{G}} e^{i(\vec{k}+\vec{G})\cdot\vec{x}}\int_0^{\eta} d\rho\ \frac{e^{-|\vec{k}+\vec{G}|^2/4\rho^2}}{\rho^3}$$
$$+\frac{2}{\sqrt{\pi}}\sum_{\ell} e^{i\vec{k}\cdot\vec{R}(\ell)}\int_{\eta}^{\infty} d\rho\ e^{-\rho^2|\vec{R}(\ell)-\vec{x}|^2}\ . \tag{D-23}$$

The first integral can be evaluated with the substitution

$$x = \frac{|\vec{k}+\vec{G}|^2}{4\rho^2} \qquad \text{(D-24)}$$

so that

$$\int_0^{\eta} d\rho \, \frac{e^{-|\vec{k}+\vec{G}|^2/4\rho^2}}{\rho^3} = \frac{2}{|\vec{k}+\vec{G}|^2} \, e^{-|\vec{k}+\vec{G}|^2/4\eta^2} \; . \qquad \text{(D-25)}$$

Using the definition of the complimentary error function

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} dt \; e^{-t^2} \; , \qquad \text{(D-26)}$$

the second integral in Eq. (D-23) is

$$\frac{2}{\sqrt{\pi}} \int_{\eta}^{\infty} d\rho \; e^{-|\vec{R}(\ell)-\vec{x}|^2 \rho^2} = \frac{\mathrm{erfc}(\eta|\vec{R}(\ell)-\vec{x}|)}{|\vec{R}(\ell)-\vec{x}|} \; . \qquad \text{(D-27)}$$

Using Eqs. (D-25) and (D-27) we have from Eq. (D-23)

$$H(\vec{k},\vec{x}) = \frac{4\pi}{\Omega_0} \sum_{\vec{G}} \frac{e^{i(\vec{k}+\vec{G})\cdot\vec{x}}}{|\vec{k}+\vec{G}|^2} \, e^{-|\vec{k}+\vec{G}|^2/4\eta^2}$$

$$+ \sum_{\ell} \frac{\mathrm{erfc}(\eta|\vec{R}(\ell)-\vec{x}|)}{|\vec{R}(\ell)-\vec{x}|} \, e^{i\vec{k}\cdot\vec{R}(\ell)} \; . \qquad \text{(D-28)}$$

In Eq. (D-28) rapid convergence of both sums can be obtained by a proper choice of the separation parameter η . Using Eqs. (D-4) and (D-12) we perform the differentiation on Eq. (D-28) to obtain

$$A_{\alpha\beta}(\vec{k},\vec{x}) = \frac{4\pi}{\Omega_o}\sum_{\vec{G}} \frac{(k_\alpha+G_\alpha)(k_\beta+G_\beta)}{|\vec{k}+\vec{G}|^2}\, e^{i(\vec{k}+\vec{G})\cdot\vec{x}}\, e^{-|k+G|^2/4\eta^2}$$

$$+ \frac{2}{\sqrt{\pi}}\sum_{\ell} e^{i\vec{k}\cdot\vec{R}(\ell)}\int_\eta^\infty d\rho[2\rho^2\delta_{\alpha\beta}-4\rho^4(R_\alpha(\ell)-x_\alpha) \times$$

$$\times (R_\beta(\ell)-x_\beta)]e^{-|\vec{R}(\ell)-\vec{x}|^2\rho^2} \qquad \text{(D-29)}$$

using the integral representation

$$\frac{1}{|\vec{x}|} = \frac{2}{\sqrt{\pi}}\int_0^\infty d\rho\; e^{-\rho^2|\vec{x}|^2} , \qquad \text{(D-30)}$$

we find upon differentiation that

$$\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\frac{1}{|\vec{x}|} = -\frac{2}{\sqrt{\pi}}\int_0^\infty d\rho(2\rho^2\delta_{\alpha\beta}-4\rho^4 x_\alpha x_\beta)e^{-|\vec{x}|^2\rho^2} . \qquad \text{(D-31)}$$

Using Eqs. (D-29) and (D-31) Eq. (D-9) becomes

$$Q^{(1)}_{\alpha\beta}(\vec{k}) = \sum_{\vec{G}}\frac{(G_\alpha-k_\alpha)(G_\beta-k_\beta)}{|\vec{G}-\vec{k}|^2}\, e^{-|\vec{G}-\vec{k}|^2/4\eta^2}$$

$$+ \frac{\Omega_o}{2\pi^{3/2}}\sum_{\ell}{}' e^{-i\vec{k}\cdot\vec{R}(\ell)}\int_\eta^\infty d\rho[2\rho^2\delta_{\alpha\beta}-4\rho^4 R_\alpha(\ell)R_\beta(\ell)]e^{-|\vec{R}(\ell)|^2\rho^2}$$

$$+ \frac{\Omega_o}{2\pi^{3/2}}\lim_{\vec{x}\to 0}\left\{\begin{array}{l}\displaystyle\int_\eta^\infty d\rho[2\rho^2\delta_{\alpha\beta}-4\rho^4 x_\alpha x_\beta]e^{-|\vec{x}|^2\rho^2} \\ \displaystyle -\int_0^\infty d\rho[2\rho^2\delta_{\alpha\beta}-4\rho^4 x_\alpha x_\beta]e^{-|\vec{x}|^2\rho^2}\end{array}\right\} . \qquad \text{(D-32)}$$

Taking the limit in the last term of Eq. (D-32) we obtain

$$Q^{(1)}_{\alpha\beta}(\vec{k}) = \frac{k_\alpha k_\beta}{|\vec{k}|^2}\, e^{-|\vec{k}|^2/4\eta^2} + \sum_{\vec{G}}{}' \frac{(G_\alpha - k_\alpha)(G_\beta - k_\beta)}{|\vec{G}-\vec{k}|^2}\, e^{-|\vec{G}-\vec{k}|^2/4\eta^2}$$

$$+ \frac{\Omega_o}{2\pi^{3/2}} \sum_{\ell}{}' e^{-i\vec{k}\cdot\vec{R}(\ell)} \int_\eta^\infty d\rho \left[2\rho^2 \delta_{\alpha\beta} - 4\rho^4 R_\alpha(\ell) R_\beta(\ell)\right] e^{-|R(\ell)|^2 \rho^2}$$

$$- \frac{\Omega_o \eta^3}{3\pi^{3/2}}\, \delta_{\alpha\beta} \ . \qquad \text{(D-33)}$$

Where we have explicitly separated out the nonanalytic $\vec{G} = 0$ term from the sum on $\vec{G}$.[2] Note also that the sum on ℓ omits the $\ell = 0$ term.

Similarly, using Eqs. (D-11) and (D-29) we obtain

$$Q^{(2)}_{\alpha\beta}(\vec{k}) = \frac{k_\alpha k_\beta}{|\vec{k}|^2}\, e^{-i\vec{k}\cdot\vec{R}(1)} e^{-|\vec{k}|^2/4\eta^2}$$

$$+ \sum_{\vec{G}}{}' \frac{(G_\alpha - k_\alpha)(G_\beta - k_\beta)}{|\vec{G}-\vec{k}|^2}\, e^{i(\vec{G}-\vec{k})\cdot\vec{R}(1)} e^{-|\vec{G}-\vec{k}|^2/4\eta^2}$$

$$+ \frac{\Omega_o}{2\pi^{3/2}} \sum_{\ell} e^{-i\vec{k}\cdot\vec{R}(\ell)} \int_\eta^\infty d\rho \left[2\rho^2 \delta_{\alpha\beta} - 4\rho^4 (R_\alpha(\ell) - R_\alpha(1))(R_\beta(\ell) - R_\beta(1))\right]$$

$$\times\, e^{-|\vec{R}(\ell) - \vec{R}(1)|^2 \rho^2} \ . \qquad \text{(D-34)}$$

Eqs. (D-33) and (D-34) can be rewritten as

$$Q_{\alpha\beta}^{(1)}(\vec{k}) = \frac{k_\alpha k_\beta}{|\vec{k}|^2}\, e^{-|\vec{k}|^2/4\eta^2} + \sum_{\vec{G}}{}' \frac{(G_\alpha - k_\alpha)(G_\beta - k_\beta)}{|\vec{G}-\vec{k}|^2}\, e^{-|\vec{G}-\vec{k}|^2/4\eta^2}$$

$$+ \frac{1}{2\pi} \sum_{\ell}{}' e^{-i\vec{k}\cdot\vec{R}(\ell)}\, I_{\alpha\beta}^{(1)}(\ell,\eta) - \frac{\Omega_o \eta^3}{3\pi^{3/2}}\, \delta_{\alpha\beta} \qquad \text{(D-35)}$$

and

$$Q_{\alpha\beta}^{(2)}(\vec{k}) = \frac{k_\alpha k_\beta}{|\vec{k}|^2}\, e^{-i\vec{k}\cdot\vec{R}(1)} e^{-|\vec{k}|^2/4\eta^2}$$

$$+ \sum_{\vec{G}}{}' \frac{(G_\alpha - k_\alpha)(G_\beta - k_\beta)}{|\vec{G}-\vec{k}|^2}\, e^{i(\vec{G}-\vec{k})\cdot\vec{R}(1)} e^{-|\vec{G}-\vec{k}|^2/4\eta^2}$$

$$+ \frac{1}{2\pi} \sum_{\ell} e^{i\vec{k}\cdot\vec{R}(\ell)}\, I_{\alpha\beta}^{(2)}(\ell,\eta) \qquad \text{(D-36)}$$

where we have defined

$$I_{\alpha\beta}^{(1)}(\ell,\eta) = \frac{\Omega_o}{\sqrt{\pi}} \int_\eta^\infty d\rho \left[2\rho^2 \delta_{\alpha\beta} - 4\rho^4 R_\alpha(\ell) R_\beta(\ell)\right] e^{-|\vec{R}(\ell)|^2 \rho^2}$$

(D-37a)

and

$$I_{\alpha\beta}^{(2)}(\ell,\eta) = \frac{\Omega_o}{\sqrt{\pi}} \int_\eta^\infty d\rho \Big[2\rho^2 \delta_{\alpha\beta} - 4\rho^4 (R_\alpha(\ell) + R_\alpha(1)) \times$$

$$\times (R_\beta(\ell) + R_\beta(1))\Big] e^{-|\vec{R}(\ell)+\vec{R}(1)|^2 \rho^2} . \qquad \text{(D-37b)}$$

Using the integrals

$$\frac{2}{\sqrt{\pi}}\int_x^{\infty} dt\ t^2 e^{-\alpha^2 t^2} = \left[\frac{x}{\sqrt{\pi}\,\alpha^2}\, e^{-\alpha^2 x^2} + \frac{1}{2\alpha^3}\,\mathrm{erfc}(\alpha x)\right] \tag{D-38}$$

$$\frac{2}{\sqrt{\pi}}\int_x^{\infty} dt\ t^4 e^{-\alpha^2 t^2} = \left(\frac{3x}{2\sqrt{\pi}\,\alpha^4} + \frac{x^3}{\sqrt{\pi}\,\alpha^2}\, e^{-\alpha^2 x^2}\right) + \frac{3}{4\alpha^5}\,\mathrm{erfc}(\alpha x) \tag{D-39}$$

we can rewrite Eqs. (D-37) as

$$I^{(1)}_{\alpha\beta}(\ell,\eta) = \frac{\Omega_0}{2}\,\Omega_{\alpha\beta}(\ell,0|0,0)\,\mathrm{erfc}(\eta|\vec{R}(\ell)|) + \frac{\Omega_0}{\sqrt{\pi}}\left[\frac{\eta\delta_{\alpha\beta}}{|\vec{R}(\ell)|^2} - \frac{R_\alpha(\ell)R_\beta(\ell)}{|\vec{R}(\ell)|^2}\left(\frac{3\eta}{|\vec{R}(\ell)|^2} + 2\eta^3\right)\right] e^{-\eta^2|\vec{R}(\ell)|^2} \tag{D-40a}$$

$$\begin{aligned} I^{(2)}_{\alpha\beta}(\ell,\eta) = {} & \frac{\Omega_0}{2}\,\Omega_{\alpha\beta}(\ell,1|0,0)\,\mathrm{erfc}(\eta|\vec{R}(\ell)+\vec{R}(1)|) \\ & + \frac{\Omega_0}{\sqrt{\pi}}\left[\frac{\eta\delta_{\alpha\beta}}{|\vec{R}(\ell)+\vec{R}(1)|^2} - \frac{(R_\alpha(\ell)+R_\alpha(1))(R_\beta(\ell)+R_\beta(1))}{|\vec{R}(\ell)+\vec{R}(1)|^2}\right. \\ & \left.\times\left(\frac{3\eta}{|\vec{R}(\ell)+\vec{R}(1)|^2} + 2\eta^3\right)\right] e^{-\eta^2|\vec{R}(\ell)+\vec{R}(1)|^2} \, . \end{aligned} \tag{D-40b}$$

Eqs. (D-35), (D-36) and (D-40) can now be used to compute the sums Eqs. (D-1) and (D-2). All that remains is to choose an appropriate value for the separation parameter

η . We have found that $\eta = \frac{2\sqrt{2}}{a}$ gives near optimum convergence for the diamond structure.

REFERENCES FOR APPENDIX D

1.) J.M. Ziman, Principles of the Theory of Solids second edition, (Cambridge Univ. Press, Cambridge, 1972) p. 7-8.

2.) A. Aharony and M.E. Fisher, Phys. Rev. B8, 3323, (1973).

Appendix E

SOME PROPERTIES OF THE DIPOLE CONTRIBUTION TO THE DYNAMICAL MATRIX

In this appendix we examine some properties of certain dipole sums. We begin by considering the dipoles induced by the homogeneous deformation

$$u_\alpha(\ell\kappa) = \sum_\beta \epsilon_{\alpha\beta} R_\beta(\ell\kappa) + d_\alpha(\kappa) \ , \tag{E-1}$$

where $\epsilon_{\alpha\beta}$ are the deformation parameters and $d_\alpha(\kappa)$ are the inner displacements.[1] Substituting Eq. (E-1) into Eqs. (1.149) and using Eqs. (1.62), (1.4) and (1.5) we obtain

$$\begin{aligned} p_\alpha(\ell,0) = & \sum_\beta \sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1)[d_\beta(1)-d_\beta(0)] \\ & + \sum_{\beta\gamma} \epsilon_{\beta\gamma} \sum_{i=1}^{4} p_{\alpha\beta}(0,0|\delta_i,1) R_\gamma(\delta_i,1) \ , \end{aligned} \tag{E-2}$$

and

$$p_\alpha(\ell,1) = -p_\alpha(\ell,0) \ . \tag{E-3}$$

Note at this point that the dipoles induced by the homogeneous deformation are independent of the unit cell index so we can write

$$p_\alpha(\ell,0) = p_\alpha \ . \tag{E-4}$$

For the important special case of an isotropic homogeneous deformation where

$$\epsilon_{\alpha\beta} = \epsilon\,\delta_{\alpha\beta} \ , \tag{E-5}$$

and

$$d_\alpha(\kappa) = 0 \ , \tag{E-6}$$

it is easy to verify using Eqs. (1.150) that p_α is zero for this deformation. Thus an isotropic deformation does not induce any dipoles and no attendant interaction energy. This being the case, it is easy to see why the dipole interaction does not affect the bulk modulus of the crystal.

Returning to the more general case and substituting Eqs. (E-3) and (E-4) into Eqs. (1.153-1.155), we obtain for the dipole-dipole interaction energy due to the deformation, Eq. (E-1), that

$$\Phi^{dd} = \frac{1}{\epsilon_s} \sum_{\alpha\beta} p_\alpha p_\beta \sum_{\ell\ell'}{}' [\Omega_{\alpha\beta}(\ell,0|\ell',0) - \Omega_{\alpha\beta}(\ell,0|\ell',1)] \ . \tag{E-7}$$

In obtaining Eq. (E-7) we have used the fact that

$$\sum_{\ell\ell'} \Omega_{\alpha\beta}(\ell,0|\ell',1) = \sum_{\ell\ell'} \Omega_{\alpha\beta}(\ell,1|\ell',0) \ , \tag{E-8}$$

which follows from relabeling the sum indices and the property

$$\Omega_{\alpha\beta}(\ell\kappa|\ell'\kappa') = \Omega_{\alpha\beta}(\ell'\kappa'|\ell\kappa) \ . \tag{E-9}$$

Defining

$$G^{(1)}_{\alpha\beta} = \sum_{\ell\ell'}{}' \; \Omega_{\alpha\beta}(\ell,0|\ell',0) \ , \qquad \text{(E-10)}$$

$$G^{(2)}_{\alpha\beta} = \sum_{\ell\ell'} \Omega_{\alpha\beta}(\ell,0|\ell',1) \ , \qquad \text{(E-11)}$$

we only need show that these terms are zero for an infinite crystal to show that the homogeneous deformation, Eq. (E-1), produces no dipole-dipole interaction energy. This being the case it then follows that the dipoles do not contribute to any of the elastic constants. We now proceed to show that $G^{(1)}_{\alpha\beta}$ and $G^{(2)}_{\alpha\beta}$ are zero for an infinite crystal. First note that translation invariance allows a relabeling of the sums so that

$$G^{(1)}_{\alpha\beta} = \sum_{\ell\ell'}{}' \; \Omega_{\alpha\beta}(\ell,0|0,0) \qquad \text{(E-12)}$$

$$G^{(2)}_{\alpha\beta} = \sum_{\ell\ell'} \Omega_{\alpha\beta}(\ell,1|0,0) \ . \qquad \text{(E-13)}$$

Next consider the sum

$$L_{\alpha\beta}(\kappa) = \sum_{\ell}{}' \; \Omega_{\alpha\beta}(\ell\kappa|0,0) \ . \qquad \text{(E-14)}$$

The diagonal terms are easily shown to be zero since using Eq. (1.154)

$$L_{11}(\kappa) = \sum_{\ell}{}' \frac{[R_1^2(\ell\kappa)+R_2^2(\ell\kappa)+R_3^2(\ell\kappa)-3R_1^2(\ell\kappa)]}{|\vec{R}(\ell\kappa)|^5} \,. \tag{E-15}$$

Using the position vectors Eq. (1.5) and relabeling sum indices we note that

$$\sum_{\ell}{}' \frac{R_1^2(\ell\kappa)}{|\vec{R}(\ell\kappa)|^5} = \sum_{\ell}{}' \frac{R_2^2(\ell\kappa)}{|\vec{R}(\ell\kappa)|^5} = \sum_{\ell}{}' \frac{R_3^2(\ell\kappa)}{|\vec{R}(\ell\kappa)|^5} \,, \tag{E-16}$$

so that we have

$$L_{11}(\kappa) = 0 \,. \tag{E-17}$$

Similar reasoning applies to show that

$$L_{22}(\kappa) = L_{33}(\kappa) = 0 \,. \tag{E-18}$$

Now consider the off-diagonal term

$$L_{12}(\kappa) = \sum_{\ell}{}' - \frac{3R_1(\ell\kappa)R_2(\ell\kappa)}{|\vec{R}(\ell\kappa)|^5} \,. \tag{E-19}$$

To show that this sum is zero, we can use a parity argument. Noting that we can relabel the summation variables by the transformation

$$R_1(\ell\kappa) = R_1(\ell'\kappa) \tag{E-20a}$$

$$R_2(\ell\kappa) = -R_2(\ell'\kappa) \tag{E-20b}$$

$$R_3(\ell\kappa) = -R_3(\ell'\kappa) \,, \tag{E-20c}$$

we have the new variables

$$\ell_1' = \ell_3 \tag{E-21a}$$

$$\ell_2' = -(\ell_1+\ell_2+\ell_3+\kappa) \tag{E-21b}$$

$$\ell_3' = \ell_1 \ . \tag{E-21c}$$

Noting that

$$|\vec{R}(\ell\kappa)| = |\vec{R}(\ell'\kappa)| \ , \tag{E-22}$$

we have that

$$L_{12}(\kappa) = \sum_{\ell}{}' + \frac{3R_1(\ell\kappa)R_2(\ell\kappa)}{|\vec{R}(\ell\kappa)|^5} \ , \tag{E-23}$$

so that

$$L_{12}(\kappa) = -L_{12}(\kappa) = 0 \ . \tag{E-24}$$

Similar arguments apply to the other off-diagonal elements so that

$$L_{\alpha\beta}(\kappa) = 0 \ . \tag{E-20}$$

Since

$$G_{\alpha\beta}^{(1)} = \sum_{\ell} L_{\alpha\beta}(0) \tag{E-21}$$

$$G_{\alpha\beta}^{(2)} = \sum_{\ell} L_{\alpha\beta}(1) \ , \tag{E-22}$$

we have that

$$G^{(1)}_{\alpha\beta} = G^{(2)}_{\alpha\beta} = 0 \ . \tag{E-23}$$

Thus we find that under the homogeneous deformation, Eq. (E-1),

$$\phi^{dd} = 0 \ .$$

Since the homogeneous deformation produces no dipole contribution to the potential energy, one can conclude that the elastic constants are not affected by the nonlocal dipole-dipole interaction. This is so since a homogeneous deformation is sufficient to determine the elastic constants.[2]

It is now easy to show that the Raman frequency is also unaffected by the nonlocal dipoles. From Eqs. (1.159) and (1.161-1.164) we obtain at $\vec{k} = 0$ that

$$\begin{aligned} D^{dd}_{\alpha\beta}(0,0|\vec{k}=0) &= \frac{32p_1^2}{\epsilon_s M} \sum_{\ell}{}' \ \Omega_{\alpha\beta}(\ell,0|0,0) \\ &\quad - \frac{32p_1^2}{\epsilon_s M} \sum_{\ell} \Omega_{\alpha\beta}(\ell,1|0,0) \ , \end{aligned} \tag{E-24}$$

and

$$D^{dd}_{\alpha\beta}(0,0|\vec{k}=0) = -D^{dd}_{\alpha\beta}(0,1|\vec{k}=0) \ . \tag{E-25}$$

Using Eqs. (E-14) and (E-20) we have

$$D^{dd}_{\alpha\beta}(\kappa\kappa'|\vec{k}=0) = 0 \ . \tag{E-26}$$

Thus we see that the dipoles do not contribute to the Raman frequency.

Similar types of symmetry arguments can be used to show the properties stated in Chapter 1, though the details are too lengthy to present here.

REFERENCES FOR APPENDIX E

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2.) P.N. Keating, Phys. Rev., <u>145</u>, 637 (1966).

Appendix F

PROOF THAT $\Phi_\alpha^{(1)}(\ell\kappa)$ AND $\Phi_\alpha^{(2)}(\ell\kappa)$ ARE ZERO IN THE DIAMOND STRUCTURE

We begin by showing that $\Phi_\alpha^{(1)}(\ell\kappa)$ has the same transformation properties as the first order atomic force constants. This is obviously true since an isotropic homogeneous deformation does not change the symmetry of the crystal.

Using the definition Eq. (2.23c)

$$\Phi_\alpha^{(1)}(LK) = \sum_{L'K'\beta} \Phi_{\alpha\beta}(LK|L'K')R_\beta(L'K') \;, \qquad \text{(F-1)}$$

we apply the transformation law Eq. (1.35) for the second order force constants under the symmetry operation Eq. (1.34) to obtain

$$\Phi_\alpha^{(1)}(LK) = \sum_{\ell'\kappa'\beta} \left[\sum_{\mu\nu} S_{\alpha\mu} S_{\beta\nu} \Phi_{\mu\nu}(\ell\kappa|\ell'\kappa')\right] \times$$
$$\times \left[\sum_\sigma S_{\beta\sigma} R_\sigma(\ell'\kappa') + v_\beta(S) + R_\beta(m)\right] \;, \qquad \text{(F-2)}$$

or

$$\Phi_\alpha^{(1)}(LK) = \sum_{\ell'\kappa'\beta} \sum_{\mu\nu\sigma} S_{\alpha\mu} S_{\beta\nu} S_{\beta\sigma} \Phi_{\mu\nu}(\ell\kappa|\ell'\kappa') R_\sigma(\ell'\kappa')$$
$$+ \sum_{\ell'\kappa'\beta} \sum_{\mu\nu} S_{\alpha\mu} S_{\beta\nu} \Phi_{\mu\nu}(\ell\kappa|\ell'\kappa') [v_\beta(S) + R_\beta(m)] \;. \qquad \text{(F-3)}$$

Using the infinitesimal translation invariance condition[1]

$$\sum_{\ell'\kappa'} \Phi_{\alpha\beta}(\ell\kappa|\ell'\kappa') = 0 , \tag{F-4}$$

Eq. (F-3) becomes

$$\Phi^{(1)}_{\alpha}(LK) = \sum_{\ell'\kappa'\beta} \sum_{\mu\nu\sigma} S_{\alpha\mu} S_{\beta\nu} S_{\beta\sigma} \Phi_{\mu\nu}(\ell\kappa|\ell'\kappa') R_{\sigma}(\ell'\kappa') . \tag{F-5}$$

Now we note that since $\overset{\leftrightarrow}{S}$ is a real orthogonal matrix

$$\sum_{\beta} S_{\beta\nu} S_{\beta\sigma} = \sum_{\beta} S^{-1}_{\nu\beta} S_{\beta\sigma} = \delta_{\nu\sigma} , \tag{F-6}$$

therefore

$$\Phi^{(1)}_{\alpha}(LK) = \sum_{\ell'\kappa'} \sum_{\mu\nu\sigma} S_{\alpha\mu} \delta_{\nu\sigma} \Phi_{\mu\nu}(\ell\kappa|\ell'\kappa') R_{\sigma}(\ell'\kappa') , \tag{F-7}$$

or

$$\Phi^{(1)}_{\alpha}(LK) = \sum_{\mu} S_{\alpha\mu} \sum_{\ell'\kappa'\nu} \Phi_{\mu\nu}(\ell\kappa|\ell'\kappa') R_{\nu}(\ell'\kappa') . \tag{F-8}$$

By the definition Eq. (F-1)

$$\Phi^{(1)}_{\mu}(\ell\kappa) = \sum_{\ell'\kappa'\nu} \Phi_{\mu\nu}(\ell\kappa|\ell'\kappa') R_{\nu}(\ell'\kappa') , \tag{F-9}$$

so that

$$\Phi_\alpha^{(1)}(LK) = \sum_\mu S_{\alpha\mu}\Phi_\mu^{(1)}(\ell\kappa) \ . \tag{F-10}$$

Eq. (F-10) is the same transformation law obeyed by the first order atomic force constants.[2] Similar reasoning can be used to show that $\Phi_\alpha^{(2)}(\ell\kappa)$ as defined by Eq. (2.23d) transforms as

$$\Phi_\alpha^{(2)}(LK) = \sum_\mu S_{\alpha\mu}\Phi_\alpha^{(2)}(\ell\kappa) \ . \tag{F-11}$$

Now that we have established the transformation law, we apply the inversion operation Eqs. (1.36) and (1.37) to obtain

$$\Phi_\alpha^{(1)}(-\ell,1) = -\Phi_\alpha^{(1)}(\ell,0) \ . \tag{F-12}$$

Lattice translation invariance gives

$$\Phi_\alpha^{(1)}(\ell+m,\kappa) = \Phi_\alpha^{(1)}(\ell,\kappa) \ , \tag{F-13}$$

so that the coefficients are independent of the unit cell index

$$\Phi_\alpha^{(1)}(\ell\kappa) = \Phi_\alpha^{(1)}(0,\kappa) \ . \tag{F-14}$$

combining Eqs. (F-12) and (F-14) we have

$$\Phi_\alpha^{(1)}(\ell,0) = \Phi_\alpha^{(1)}(0,0) = -\Phi_\alpha^{(1)}(0,1) = -\Phi_\alpha^{(1)}(\ell,1) \ . \tag{F-15}$$

The simple two-fold rotation element[3] δ_{2x}

$$\overleftrightarrow{S}_{\delta_{2x}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} , \qquad \text{(F-16)}$$

gives

$$\Phi_2^{(1)}(0,0) = -\Phi_2^{(1)}(0,0) = 0 , \qquad \text{(F-17a)}$$

and

$$\Phi_3^{(1)}(0,0) = -\Phi_3^{(1)}(0,0) = 0 . \qquad \text{(F-17b)}$$

The further operation δ_{2y}

$$\overleftrightarrow{S}_{\delta_{2y}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} , \qquad \text{(F-18)}$$

gives

$$\Phi_1^{(1)}(0,0) = -\Phi_1^{(1)}(0,0) = 0 . \qquad \text{(F-19)}$$

Eqs. (F-17) and (F-19) together with Eq. (F-15) show that

$$\Phi_\alpha^{(1)}(\ell\kappa) = 0 . \qquad \text{(F-20)}$$

Since $\Phi_{\alpha}^{(2)}(\ell\kappa)$ obeys the same transformation law, it follows that it also is zero in the diamond structure. Note that the proof only applies to an infinite crystal, since surfaces break the translation invariance condition Eq. (F-13).

REFERENCES FOR APPENDIX F

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2.) A.A. Maradudin, Ref. 1, p. 18 Eq. (2.11a).

3.) M. Lax, Symmetry Principles in Solid State and Molecular Physics, (Wiley, New York, 1974) p. 257.