MOLECULAR FORCES AND ELASTIC CONSTANTS OF POLYETHYLENE SINGLE CRYSTALS

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY

Joginder N. Anand

1966

ABSTRACT

MOLECULAR FORCES AND ELASTIC CONSTANTS OF POLYETHYLENE SINGLE CRYSTALS

by Joginder N. Anand

Lamellar polyethylene single crystals have a folded-chain structure in which planar zigzag segments of molecules take an orthorhombic lattice. For these crystals, nine independent elastic constants appear in the generalized Hooke's law. Thus, they are inherently quite anisotropic.

Their anisotropy is enhanced further by the directional intra- and intermolecular forces. Intramolecular forces are due to the covalent C-C bonds forming the chains, and are much stronger than the intermolecular London dispersion-type of van der Waals forces. The latter have been approximated by a 6-12 Lennard-Jones potential involving two unknown constants; the ratio of which is fixed by the equilibrium separation to give a minimum in the potential. Their values are determined by comparing the computed crystal potential energy and the experimentally-determined cohesive energy, and are found to be comparable with those of argon.

First and second nearest-neighbor interactions are considered to derive finite difference expressions for the components of the force acting on a unit in terms of relative displacements and interaction constants. These are converted into partial differential equations and compared with the corresponding equations of motion obtained from continuum theory to establish relationships between the elastic

constants and the interaction constants. A limited central force assumption is employed to reduce the number of interaction constants from thirty to fourteen for the second nearest-neighbors and from eleven to seven for the first neighbors only.

Interaction constants for units belonging to the same chain are obtained in terms of the C-C bond stretching, bending and repulsive force constants while others are obtained from the 6-12 potential in terms of the Lennard-Jones constants and the appropriate separation distances.

Finally, by substituting values of the intra- and intermolecular force constants and the geometric parameters, numerical values of the interaction constants and the elastic constants have been obtained. From these the values of Young's moduli E_1, E_2 and E_3 obtained in directions a, b and c, are found to be about 0.38×10^{-6}, 0.27×10^{-6} and 2.39×10^{-4} dyne/A^2 respectively; while the constants c_{44}, c_{55} and c_{66}, identified as shear moduli, have been calculated to be 1.12×10^{-4}, 0.89×10^{-4} and 6.52×10^{-7} dyne/A^2. The magnitudes of the constants c_{23}, c_{13} and c_{12} are found to be equal to those of c_{44}, c_{55} and c_{66}.

The value of E_3 for the chain direction compares well with the Young's modulus of oriented polyethylene obtained theoretically as well as experimentally. Furthermore, the value of the Young's modulus of bulk polyethylene lies between the values obtained for moduli along and across the chain. It is interesting to note that polyethylene single crystals are found to have shear resistance even when only first neighbor interactions are considered and forces are central.

MOLECULAR FORCES AND ELASTIC CONSTANTS OF POLYETHYLENE SINGLE CRYSTALS

by

Joginder N. Anand

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Metallurgy,
Mechanics and Materials Science

1966

ACKNOWLEDGEMENTS

The author is very grateful to Dr. T. Triffet for his continued guidance and assistance throughout the course of the work which made this thesis possible. He wishes to thank him for acting as thesis advisor and chairman of the guidance committee.

He also wishes to extend thanks to the members of the guidance committee for their helpful suggestions and interest in this work.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF APPENDICES

I. INTRODUCTION

1.1. Crystallinity in Polymers

It has been found that most polymers, perhaps all, are partially crystalline, having co-existing ordered and disordered regions (1). Their x-ray diffraction patterns show both sharp features associated with regions of three-dimensional order, and more diffuse features characteristic of molecularly disordered substances like liquids. The degree of crystallinity can be estimated from changes in density, specific heat, refractive index, transparency, x-ray diffraction patterns and various other physical properties. In fact, many of the unique physical properties of polymers are associated with their ability to crystallize.

Stereoregular isotactic polymers whose molecules are chemically and geometrically regular in structure, such as linear polyethylene, are typically crystalline. Noncrystalline polymers, on the other hand, include those in which irregularity of structure occurs, such as atactic polymers or copolymers with significant amount of two or more quite different monomer constituents.

Unit cell data and other information, such as the configuration or chemical structure and the conformation of several crystalline polymers, have been compiled by Miller and Nielson (2). In a number of new isotactic polymers two or more conformations and unit cells have been observed to depend upon the temperature and other conditions of crystallization. The most commonly occurring unit cell structures in various polymers may be classified as orthorhombic, pseudoorthorhombic, triclinic, hexagonal, monoclinic and rhombohedral.

1.2. Polymer Single Crystals and Related Structures

Crystalline polymers usually crystallize from dilute solutions in the form of thin lamellae called single crystals; and such crystals of many polymers such as gutta-percha, polyethylene, polypropylene, polyamides, cellulose and its derivatives have been reported since their independent discovery and identification in 1957 by Till (3), Keller (4), and Fischer (5). All polymer crystals have the same general appearance, being composed of thin, flat or hollow pyramidal platelets. Spiral growths of additional lamellae originating from screw dislocations are usually present on their surface. Crystallization conditions such as solvent, solvent concentration, temperature and rate of cooling determine the size, shape and regularity of these crystals. However, their thickness depends mainly on the crystallization temperature and any subsequent annealing treatment (6).

Electron diffraction analyses of these crystals indicate that the polymer chains are normal or nearly normal to the plane of the lamellae (3, 4, 5). The length of polymer chains being several times the thickness of a lamella, Keller (4) points out that the molecules must be folded back and forth on themselves several times. In polyethylene, for instance, the molecules can fold in such a way that only five carbon atoms are involved in the fold itself (6), as shown in Figure 1.4 (b).

When the rate of growth during crystallization is slow, relatively thick aggregates of single crystal lamellae having a common nucleus and orientation, called hedrites (Figure 1.5 c), have been reported for polyethylene and polyoxymethylene (7, 8, 6). They have a polygonal appearance, and are the closest approach to a macroscopic single crystal. But at faster growth rates numerous defects, such as vacancies and interstitials, terminal groups, branches and improper folds, are incorporated into the lattice.

During crystallization from the melt spherulites develop which have a complex lamellar structure, as seen in the electron microscope (9). Their nuclei have a random orientation, and growth occurs radially outward from these until the entire volume is filled. When two spherulites meet during crystallization they form a common straight boundary in which the transition in orientation takes places (1).

This picture, known as the "crystal defect solid" model of crystalline polymers, visualizes the matrix as an ordered region having defects incorporated throughout (1). It is in direct contrast to the old "fringed micelle" concept, in which a crystalline phase consisting of crystallites is taken to be embeded in an amorphous matrix forming a second phase. In the latter, molecular chains are visualized to pass through several crystallites and, thus, to have several straight and several disordered segments, as shown in Figure 1.1.

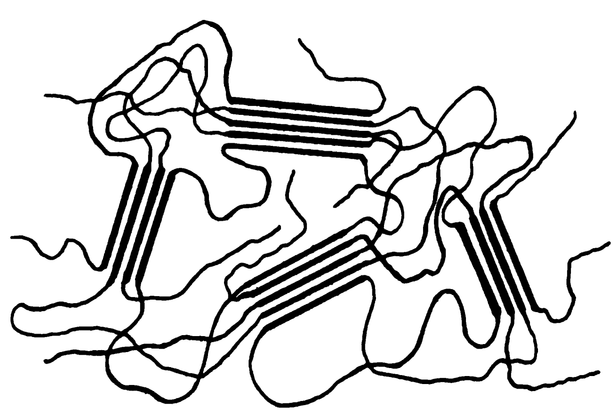


Figure 1.1. Fringed micelle model.

though

nstall

script

.1. P

The

ethylene

eflecti

shown b

This m

exist

hydro

longe

and i

at the

Although from a macroscopic point of view it may appear that at low crystallinities both concepts are identical, as far as a microscopic description is concerned the two are completely different.

1.3. Polyethylene and Its Single Crystal Structure

The chemical formula of polyethylene is C_nH_{2n+2}. Thus, a polyethylene molecular chain consists of n, $-CH_2-$ chemical repeat units, neglecting the end ones. The configuration of a linear molecule is shown below in Figure 1.2.

```
  H  H  H  H  H  H
  |  |  |  |  |  |
H-C -C -C -C -C -C -
  |  |  |  |  |  |
  H  H  H  H  H  H
```

Figure 1.2. Configuration of linear polyetheylene.

This may also be abbreviated and written as $(-CH_2-)_n$.

Covalent single bonds formed by the sharing of two electrons, exist between two consecutive carbon atoms and between carbon and hydrogen atoms. The length of the C-C bond is about 1.54A, slightly longer than the C-H bond length of about 1.10A. Carbon is tetravalent and its four bonds are directed in space in such a manner that it lies at the center of a tetrahedron as shown in Figure 1.3.

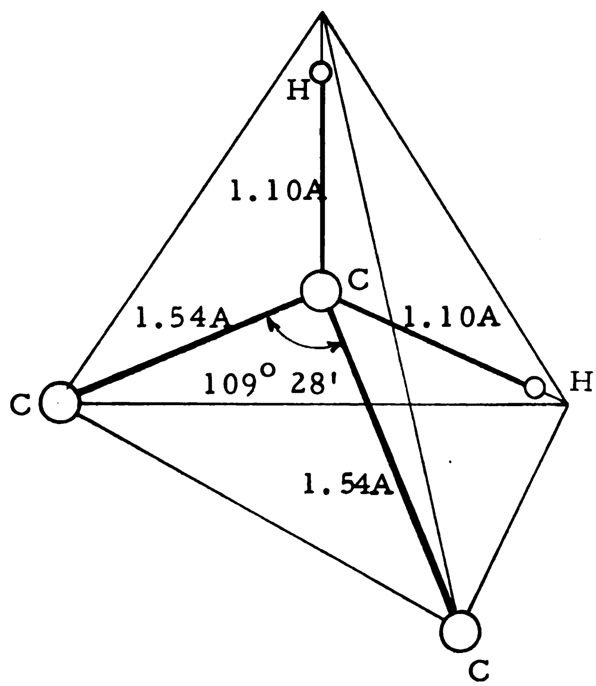


Figure 1.3. Tetrahedron formed by the four bonds of carbon.

The angle between any two bonds is approximately the tetrahedral angle of 109°28', as shown. Carbon atoms forming the backbone of a linear polyethylene molecule take up a planar zigzag conformation when in a crystal lattice, as shown in Figure 1.4 (a).

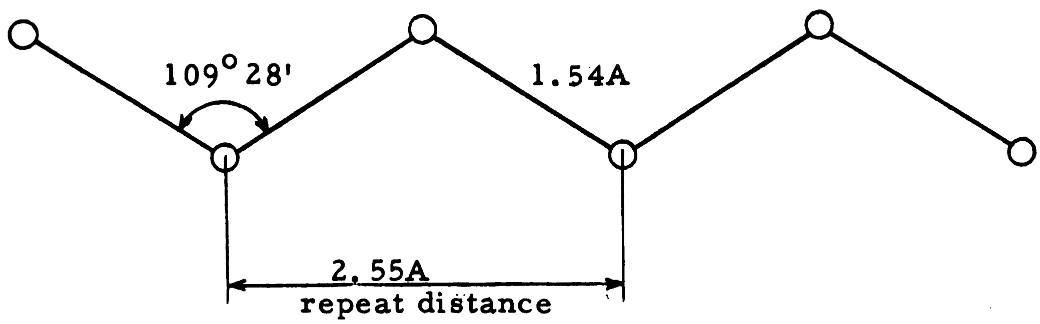


Figure 1.4(a). Planar zigzag conformation.

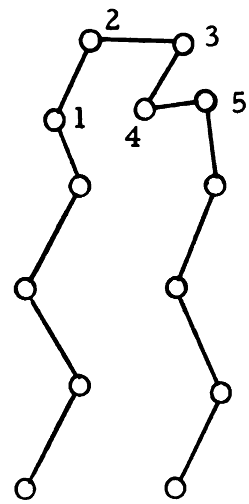


Figure 1.4(b). Chain folding involving five C atoms.

The repeat unit is $(-CH_2-CH_2-)$ or $(-C_2H_4-)$ and the distance between two alternate C atoms is the repeat distance; it is approximately equal to 2.55A.

Polyethylene single crystals crystallizing from dilute solutions have well defined forms, which usually consist of lozenge-shaped flat or hollow pyramids 100-200A in thickness and about 10-20 microns in lateral dimensions:

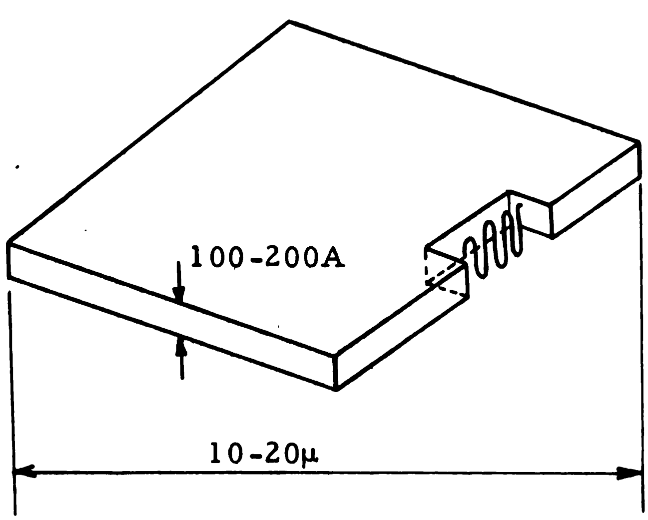
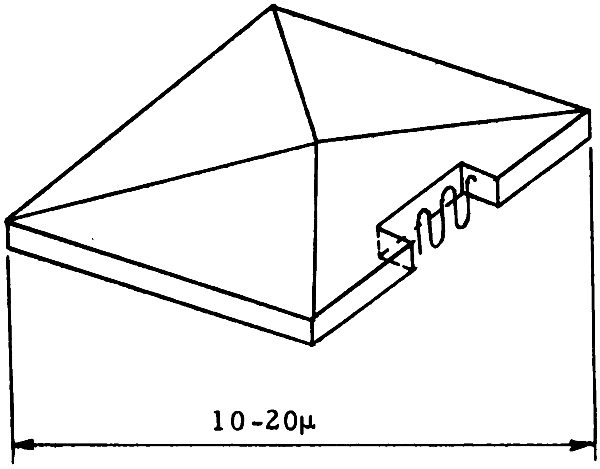
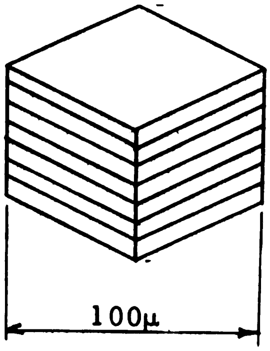


Figure 1.5(a). Schematic diagram of flat single crystal.



(b)



(c)

Figure 1.5. Schematic diagrams (b) hollow pyramid, lozenge-shaped, platelike polyethylene single crystals having a folded-chain structure (c) hedrites.

The molecular chains forming these crystals have a fold-length of the order of the thickness of the crystals (4).

The unit cell structure of polyethylene is orthorhombic, and is shown in Figure 1.6 (a, b, c).

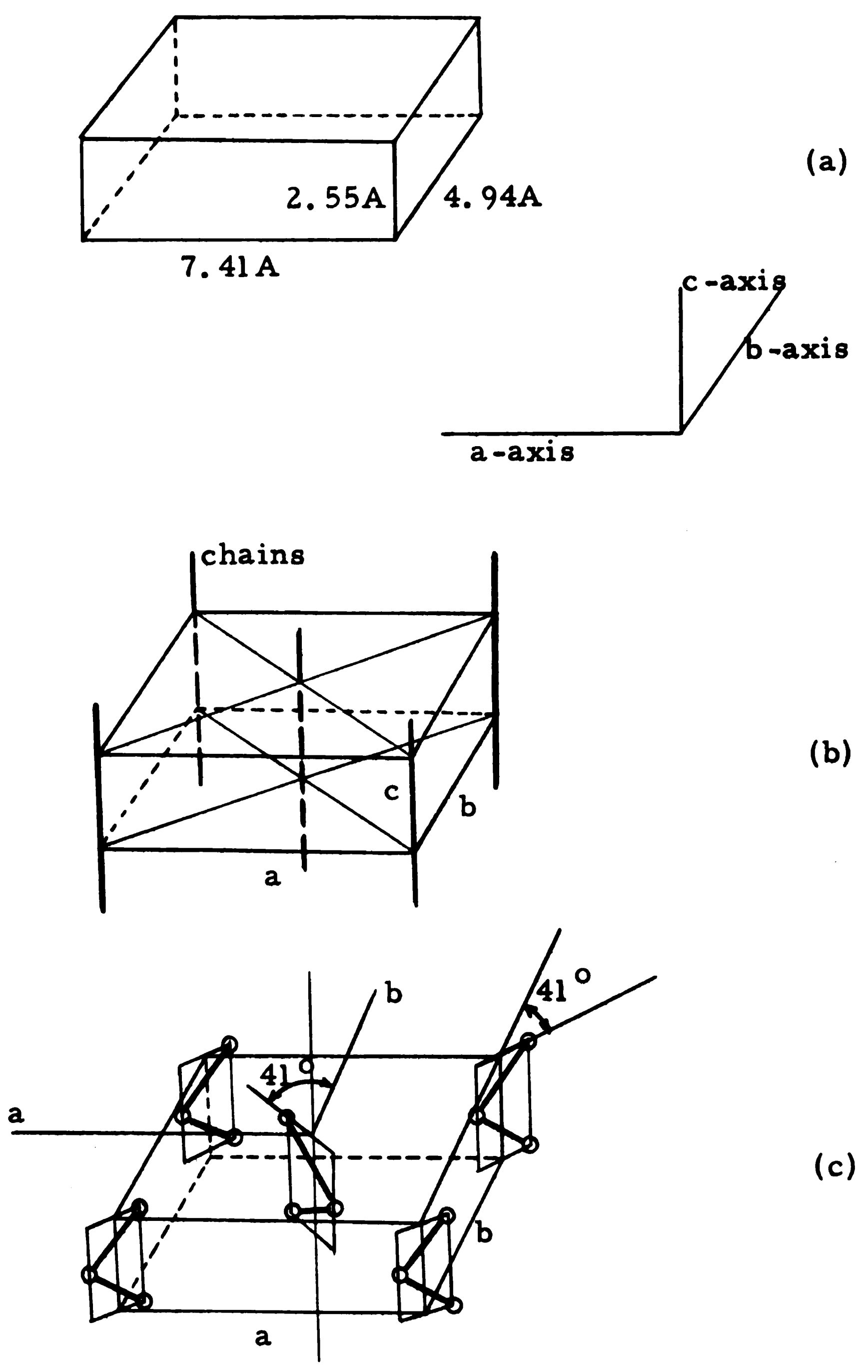


Figure 1.6. Schematic representation of the unit cell of polyethylene showing (a) parameters a, b and c (b) location of molecular chains along the c-axis and (c) setting angle of 41° that the planes of chains make with the b-axis.

ues a

nd c

as det

than

nt c

the c

maki

Summ

havin

the r

than

to fo

cons

resp

in F

Axes a, b, and c are orthogonal and the respective parameters a, b and c are approximately 7.41A, 4.94A and 2.55A at room temperature, as determined by x-ray diffraction by Cole and Holmes (10). Molecular chains lie along the c-axis, thus, c is just the repeat distance. The unit cell consists of four parallel planar zigzag chains running along the c-axis at the four corners of the (a, b) rectangle, their planes making an angle of $\beta = 41^{\circ}$, with the b-axis, as determined by Bunn (11), and one running through the mid-point of the rectangle having a different orientation from the other four. The chain through the midpoint of the rectangle and three additional similarly-oriented chains through the midpoints of adjacent rectangles may be considered to form their own (a, b) rectangle. Thus, the entire crystal may be considered to consist of chains having these two orientations, their respective rectangles forming an entangled cell structure as shown in Figure 1.7 (a and b):

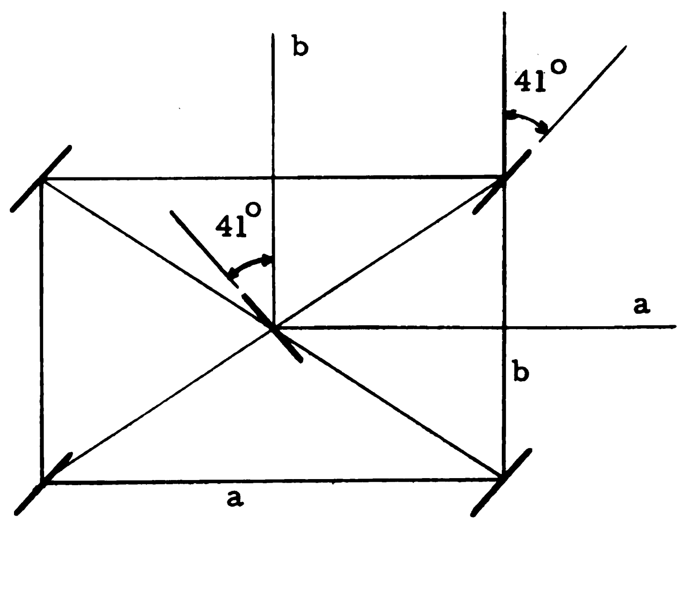


Figure 1.7(a). Entangled-rectangular cell structure.

1.4.

It con

const

Aniso

polye

meri

dire

cova

bon

van

the

1.

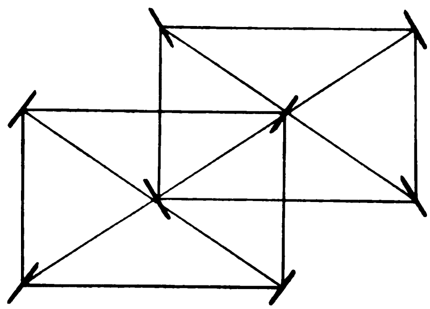


Figure 1. 7(b). Entangled-rectangular cell structure.

1. 4. Anisotropy of Polyethylene Single Crystals

For the class of crystals having an orthorhombic lattice, the 36 constants of the generalized Hooke's law are reduced to 9 independent constants, as against 3 for crystals having cubic symmetry (12). Anisotropy of such crystals is, thus, much more complex. Besides, polyethylene single crystals have another feature, peculiar to polymeric crystals, which contributes to additional anisotropy. In the direction of the c-axis, or along the molecular chains, the primary covalent C-C bonds, are several times stronger than the secondary bonds existing between any two molecular chains due to the weak van der Waals forces (13, 6). This difference is superimposed on the inherent anisotropy of the orthorhombic lattice structure.

1. 5. Objectives

A connection between the nine independent elastic constants, as they a

thermol

single cr

accompl

constant

for the f

rombic

approac

actions

is dem

in tern

torsio

exist

const

to se

vario

Sima

not

appr

two

the

the

exp

pol

as they appear in the generalized Hooke's law, and the microscopic intermolecular and intramolecular force constants is obtained for single crystals of polyethylene in the present work. However, in accomplishing this objective the continuum or macroscopic elastic constants are obtained first in terms of interaction force constants, for the forces existing between units occupying the present orthorhombic lattice, by following the von Kármán cubic crystal structure approach (14).

First nearest-neighbor and second nearest-neighbor interactions are accounted for, and the effect of central force assumption is demonstrated. The interaction force constants are in turn obtained in terms of the more basic constants, such as stretching, bending, torsion and repulsive force constants for the primary C-C bonds that exist along the molecular chain axis, and the intermolecular force constants for the net attractive forces between adjacent chains due to secondary bond forces. The strength of the C-C bonds under various types of deformation is well-established, by Mizushima and Simanouti (15). However, the strength of the secondary bonds is not known for polyethylene.

The net potential existing between adjacent chains is approximated by a 6-12 Lennard Jones potential (6), which involves two constants whose ratio is determined by the equilibrium distance of the two chains. Their exact values are then determined by calculating the crystal potential energy density and comparing it with the experimentally-determined value of the cohesive energy density for polyethylene (16).

Numerical values of the interaction constants are obtained from the values of the C-C bond strength constants, the Lennard-Jones potential constants and the geometric parameters. These are then substituted in the expressions for the elastic constants to yield their numerical values. The nine independent elastic constants of the generalized Hooke's law are measures of the Young's and shear moduli of polyethylene single crystals in various directions. These are compared with known values of the constants, such as the Young's moduli of oriented and bulk polyethylene. Shimanouchi, et al. (17) have calculated the Young's modulus for oriented polyethylene, consisting of infinitely long molecular chains, to be 3.4×10^{-4} dyne/A^2. This is somewhat higher than the value of 2.6×10^{-4} dyne/A^2 determined experimentally by Dulmage and Contois (18), using x-ray diffraction and the relaxation technique.

The values of the Young's moduli along other directions should be considerably lower than this, because the forces existing along other directions are much weaker. The Young's modulus of bulk crystalline polyethylene is of the order of 10^{-5} dyne/A^2, and this must represent some kind of an average of the moduli of polyethylene single crystals along the three lattice axes. Like the Young's moduli, the shear moduli too should be higher along the chain direction.

II. THEORETICAL DEVELOPMENTS

2.1. Elastic Constants of Polyethylene Single Crystals

In the orthorhombic lattice structure of polyethylene, as discussed in Section 1.3 and illustrated in Figures 1.6 a-c, four molecular chains having parallel orientations and one having a different orientation occupy, respectively, the four corners and the center of the rectangle (a, b). This may be reduced to a simple orthorhombic lattice by considering pairs of two chains, consisting of one at the corner and the other at the center of the rectangle, to occupy lattice points, as shown in Figure 2.1. This reduction

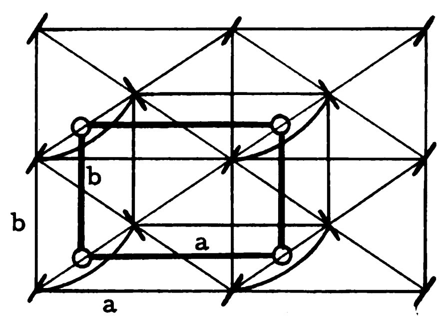


Figure 2.1. Reduction to simple orthorhombic lattice. Lattice points are occupied by units of two chains connected by a natural fold.

facilitates the application of symmetry operations to a polyethylene single crystal, since then the crystal would have the same number of symmetry elements as a simple orthorhombic lattice cell structure. It may also be noted that a chain lying along the c-axis can be broken into $(-C_2H_4-)$ repeat units without any loss of generality and, as shown in Figure 2.2, the equivalent lattice structure is then an orthorhombic structure with units occupying the lattice points.

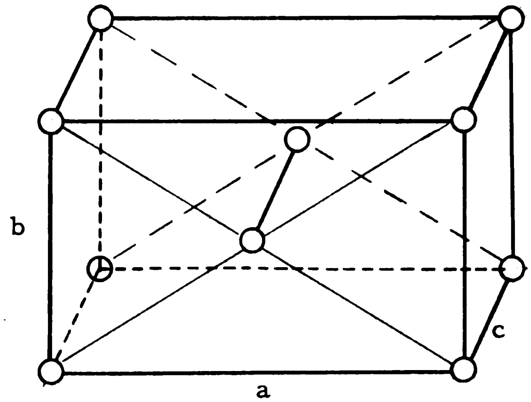


Figure 2.2. Equivalent lattice with $(-C_2H_4-)$ units occupying lattice points.

We are now in a position to write Hooke's law with proper symmetry operations for polyethylene single crystals. For small strains, Hooke's law states that stress is proportional to strain and for an anisotropic medium its generalized form may be written mathematically as

$$\sigma_i = c_{ij}\,\epsilon_j \qquad 2.1$$

The constants of proportionality c_{ij} are called the elastic constants or moduli of elasticity, while σ_i and ϵ_j respectively represent the stress and strain components. Equation 2.1 may also be solved for strains in terms of stresses to obtain

$$\epsilon_i = s_{ij}\,\sigma_j \quad , \qquad 2.2$$

and elements s_{ij} of the inverse matrix are called the moduli of compliance.

The 36 elastic constants in Equation 2.1 are reduced to only 9 independent constants (12, 19) for the symmetry elements of an orthorhombic lattice. These nine constants are shown in the matrix given below

$$c_{ij} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{21} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{31} & c_{32} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix} \qquad 2.3$$

where $c_{12} = c_{21}$, $c_{13} = c_{31}$ and $c_{23} = c_{32}$.

Equation 2.1 may now be written out by using this matrix:

$$\begin{aligned} \sigma_1 &= c_{11}\epsilon_1 + c_{12}\epsilon_2 + c_{13}\epsilon_3 \\ \sigma_2 &= c_{12}\epsilon_1 + c_{22}\epsilon_2 + c_{23}\epsilon_3 \\ \sigma_3 &= c_{13}\epsilon_1 + c_{23}\epsilon_2 + c_{33}\epsilon_3 \\ \sigma_4 &= c_{44}\epsilon_4 \\ \sigma_5 &= c_{55}\epsilon_5 \\ \sigma_6 &= c_{66}\epsilon_6 \end{aligned} \qquad 2.4$$

Letting u, v and w be the components of displacement along the axes x, y and z, respectively, where these correspond sequentially with the parametric axes a, b and c, we may write the strains ϵ_i

as

and

Also,

where

Shear

where

where

Youn

and

max

and d

as

$$\epsilon_1 = \frac{\partial u}{\partial x}, \quad \epsilon_2 = \frac{\partial v}{\partial y}, \quad \epsilon_3 = \frac{\partial w}{\partial z}$$

and 2.5

$$\epsilon_4 = \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}, \quad \epsilon_5 = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}, \quad \epsilon_6 = \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}$$

Also, it may be noted that

$$\epsilon_4 = \gamma_{23}$$

$$\epsilon_5 = \gamma_{13}$$

$$\epsilon_6 = \gamma_{12} \qquad 2.6$$

where the γ_{ij}'s are shear strains. Young's modulus E and the Shear modulus G are defined by

$$E = \frac{\sigma}{\epsilon}, \qquad 2.7$$

where σ and ϵ are the longitudinal stress and strain, and

$$G = \frac{\tau}{\gamma}, \qquad 2.8$$

where τ and γ are the shear stress and strain.

Applying this to the particular case in hand, we obtain three Young's moduli E_1, E_2, E_3, and three shear moduli G_{23}, G_{13}, and G_{12} as shown below.

Rewriting the first of the six expressions in 2.4 as for uniaxial stress σ_1 only

$$E_1\epsilon_1 = \sigma_1 = c_{11}\epsilon_1 + c_{12}\epsilon_2 + c_{13}\epsilon_3 \qquad 2.9$$

and dividing both sides by ϵ_1, we get

Similarl

express

and

Poiss

to ge

Sub

$$E_1 = c_{11} + c_{12}\frac{\epsilon_2}{\epsilon_1} + c_{13}\frac{\epsilon_3}{\epsilon_1} \quad .$$

Similarly, by repeating the above operations for the other five expressions in 2.4, we get

$$E_2 = c_{12}\frac{\epsilon_1}{\epsilon_2} + c_{22} + c_{23}\frac{\epsilon_3}{\epsilon_2} \qquad 2.10$$

$$E_3 = c_{13}\frac{\epsilon_1}{\epsilon_3} + c_{23}\frac{\epsilon_2}{\epsilon_3} + c_{33}$$

and

$$E_4 = c_{44} = G_{23}$$

$$E_5 = c_{55} = G_{13} \qquad 2.11$$

$$E_6 = c_{66} = G_{12} \quad .$$

Poisson's ratios ν_{ij} may be defined as

$$\nu_{ij} = -\frac{\epsilon_i}{\epsilon_j} = -\frac{1}{\frac{\epsilon_j}{\epsilon_i}} = \frac{1}{\nu_{ji}} \qquad 2.12$$

to get six ν_{ij}'s, such that

$$\nu_{12} = -\frac{\epsilon_1}{\epsilon_2} \ , \quad \nu_{21} = -\frac{\epsilon_2}{\epsilon_1}$$

$$\nu_{31} = -\frac{\epsilon_3}{\epsilon_1} \ , \quad \nu_{13} = -\frac{\epsilon_1}{\epsilon_3} \qquad 2.13$$

$$\nu_{23} = -\frac{\epsilon_2}{\epsilon_3} \ , \quad \nu_{32} = -\frac{\epsilon_3}{\epsilon_2} \quad .$$

Substituting 2.13 in 2.10, we obtain:

$$E_1 = c_{11} - c_{12}\,\nu_{21} - c_{13}\,\nu_{31}$$

$$E_2 = c_{22} - c_{12}\,\nu_{12} - c_{23}\,\nu_{32} \qquad 2.14$$

The w

simple

η_j al

Solvin

and s

direc

$$E_3 = c_{33} - c_{13}\,\nu_{13} - c_{23}\,\nu_{23}$$

The ν_{ij}'s may be evaluated in terms of the c_{ij}'s by using simple uniaxial stresses. Thus, considering a uniaxial stress σ_1 along the x-direction, 2.4 becomes

$$\begin{aligned} \sigma_1 &= c_{11}\,\epsilon_1 + c_{12}\,\epsilon_2 + c_{13}\,\epsilon_3 \\ 0 &= c_{12}\,\epsilon_1 + c_{22}\,\epsilon_2 + c_{23}\,\epsilon_3 \\ 0 &= c_{13}\,\epsilon_1 + c_{23}\,\epsilon_2 + c_{33}\,\epsilon_3 \end{aligned} \qquad 2.15$$

Solving the last two equations of 2.15 simultaneously, it follows that:

$$\begin{aligned} \nu_{21} &= -\frac{\epsilon_2}{\epsilon_1} = \frac{c_{33}\,c_{12} - c_{23}\,c_{13}}{c_{33}\,c_{22} - c_{23}^2} \\ \nu_{31} &= -\frac{\epsilon_3}{\epsilon_1} = \frac{c_{22}\,c_{13} - c_{12}\,c_{23}}{c_{33}\,c_{22} - c_{23}^2} \quad ; \end{aligned} \qquad 2.16$$

and similarly by considering uniaxial stresses in the x and y-directions, we obtain:

$$\begin{aligned} \nu_{32} &= -\frac{\epsilon_3}{\epsilon_2} = \frac{c_{11}\,c_{23} - c_{13}\,c_{12}}{c_{11}\,c_{33} - c_{13}^2} \\ \nu_{12} &= -\frac{\epsilon_1}{\epsilon_2} = \frac{c_{33}\,c_{12} - c_{23}\,c_{13}}{c_{33}\,c_{11} - c_{13}^2} \\ \nu_{13} &= -\frac{\epsilon_1}{\epsilon_3} = \frac{c_{22}\,c_{13} - c_{12}\,c_{23}}{c_{22}\,c_{11} - c_{12}^2} \\ \nu_{23} &= -\frac{\epsilon_2}{\epsilon_3} = \frac{c_{11}\,c_{23} - c_{12}\,c_{13}}{c_{11}\,c_{22} - c_{12}^2} \end{aligned} \qquad 2.16a$$

Simil

stres

It sh

and

obta

Substituting 2.16 in 2.14 gives:

$$E_1 = c_{11} + \frac{c_{12}(c_{23}c_{13} - c_{33}c_{12}) + c_{13}(c_{12}c_{23} - c_{22}c_{13})}{(c_{22}c_{33} - c_{23}^2)}$$

$$= c_{11} + \frac{2\, c_{12}\, c_{13}\, c_{23} - c_{12}^2\, c_{33} - c_{13}^2\, c_{22}}{(c_{22}\, c_{33} - c_{23}^2)}$$

$$= \frac{c_{11}c_{22}c_{33} + 2\, c_{12}c_{23}c_{31} - c_{12}^2 c_{33} - c_{23}^2 c_{11} - c_{31}^2 c_{22}}{(c_{22}\, c_{33} - c_{23}^2)} \qquad 2.17$$

Similarly, E_2 and E_3 may be obtained by considering uniaxial stresses σ_2 and σ_3 in the y and z-directions; they are:

$$E_2 = \frac{c_{11}c_{22}c_{33} + 2\, c_{11}c_{23}c_{31} - c_{12}^2 c_{33} - c_{23}^2 c_{11} - c_{31}^2 c_{22}}{(c_{11}\, c_{33} - c_{13}^2)} \qquad 2.18$$

$$E_3 = \frac{c_{11}c_{22}c_{33} + 2\, c_{11}c_{23}c_{31} - c_{12}^2 c_{33} - c_{23}^2 c_{11} - c_{31}^2 c_{22}}{(c_{11}\, c_{22} - c_{12}^2)} \qquad 2.19$$

It should be noted that

$$(c_{22}c_{33} - c_{23}^2)\, E_1 = (c_{11}c_{33} - c_{13}^2)\, E_2 = (c_{11}c_{22} - c_{12}^2)\, E_3$$

$$= c_{11}c_{22}c_{33} + 2\, c_{11}c_{23}c_{31} - c_{12}^2 c_{33}$$

$$- c_{23}^2 c_{11} - c_{31}^2 c_{22} \quad . \qquad 2.20$$

Later in this work expressions for the elastic strain energy and equations of motion will be needed for comparison with equations obtained from microscopic considerations, in order to evaluate the interaction force constants. To get such an expression for the elastic strain energy density U, we note that

$$\frac{\partial U}{\partial \epsilon_1} = \sigma_1 \ , \quad \frac{\partial U}{\partial \epsilon_2} = \sigma_2 \ , \quad \ldots , \tag{2.21}$$

all of which may be satisfied if U takes the following form:

$$\begin{aligned} U = {} & \frac{1}{2}(c_{11}\epsilon_1^2 + c_{22}\epsilon_2^2 + c_{33}\epsilon_3^2) \\ & + (c_{12}\epsilon_1\epsilon_2 + c_{13}\epsilon_1\epsilon_3 + c_{23}\epsilon_2\epsilon_3) \\ & + \frac{1}{2}(c_{44}\epsilon_4^2 + c_{55}\epsilon_5^2 + c_{66}\epsilon_6^2) \end{aligned} \tag{2.22}$$

Thus,

$$\begin{aligned} \frac{\partial U}{\partial \epsilon_1} &= c_{11}\epsilon_1 + c_{12}\epsilon_2 + c_{13}\epsilon_3 = \sigma_1 \\ \frac{\partial U}{\partial \epsilon_2} &= c_{12}\epsilon_1 + c_{22}\epsilon_2 + c_{23}\epsilon_3 = \sigma_2 \\ \frac{\partial U}{\partial \epsilon_3} &= c_{13}\epsilon_1 + c_{23}\epsilon_2 + c_{33}\epsilon_3 = \sigma_3 \end{aligned} \tag{2.23}$$

and

$$\frac{\partial U}{\partial \epsilon_4} = c_{44}\epsilon_4 = \sigma_4, \quad \frac{\partial U}{\partial \epsilon_5} = c_{55}\epsilon_5 = \sigma_5, \quad \frac{\partial U}{\partial \epsilon_6} = c_{66}\epsilon_6 = \sigma_6 \ ,$$

which obviously satisfy 2.21.

Now, the equations of motion may be written in the form (12, 14):

$$\rho_o \ddot{u} = \frac{\partial \sigma_1}{\partial x} + \frac{\partial \sigma_6}{\partial y} + \frac{\partial \sigma_5}{\partial z}$$

where

orthor

resul

ρ_c

ρ_o

ρ_o

const

expr

strai

invol

2.2,

and

not

disc

men

$$\rho_o \ddot{v} = \frac{\partial \sigma_6}{\partial x} + \frac{\partial \sigma_2}{\partial y} + \frac{\partial \sigma_4}{\partial z}$$

$$\rho_o \ddot{w} = \frac{\partial \sigma_5}{\partial x} + \frac{\partial \sigma_4}{\partial y} + \frac{\partial \sigma_3}{\partial z} \qquad 2.24$$

where ρ_o is the density. To specialize these equations for an orthorhombic lattice, we must substitute 2.4 and 2.5 in these; the result is:

$$\rho_o \ddot{u} = c_{11} \frac{\partial^2 u}{\partial x^2} + c_{66} \frac{\partial^2 u}{\partial y^2} + c_{55} \frac{\partial^2 u}{\partial z^2} + (c_{12}+c_{66}) \frac{\partial^2 v}{\partial x \partial y} + (c_{13}+c_{55}) \frac{\partial^2 w}{\partial x \partial z}$$

$$\rho_o \ddot{v} = c_{66} \frac{\partial^2 v}{\partial x^2} + c_{22} \frac{\partial^2 v}{\partial y^2} + c_{44} \frac{\partial^2 v}{\partial z^2} + (c_{12}+c_{66}) \frac{\partial^2 u}{\partial x \partial y} + (c_{23}+c_{44}) \frac{\partial^2 w}{\partial y \partial z}$$

$$\rho_o \ddot{w} = c_{55} \frac{\partial^2 w}{\partial x^2} + c_{44} \frac{\partial^2 w}{\partial y^2} + c_{33} \frac{\partial^2 w}{\partial z^2} + (c_{13}+c_{55}) \frac{\partial^2 u}{\partial x \partial z} + (c_{23}+c_{44}) \frac{\partial^2 v}{\partial y \partial z}$$

2.25

Since the orthorhombic lattice has nine independent elastic constants c_{ij} instead of three, like a simple cubic structure, expressions for the Young's moduli, shear moduli, Poisson's ratios, strain energy, and equations of motion are naturally much more involved.

2.2. Intramolecular and Intermolecular Force Constants

Various molecular force constants are described in this section, and a procedure is developed for calculating some of them which are not known. In Section 2.4 the macroscopic elastic constants c_{ij} discussed in Section 2.1 will be obtained in terms of the above-mentioned microscopic force constants; for this purpose the two following types of forces are important:

(i) Intramolecular or primary bond forces

(ii) Intermolecular or secondary bond forces

i) Intramolecular Forces

The carbon atoms constituting the backbone of a linear polyethylene molecule are held together by covalent bonds formed by sharing pairs of valence electrons. These C-C bonds feature the primary or intramolecular forces with which we will be concerned. The other covalent bonds are carbon-hydrogen or C-H bonds by means of which hydrogen atoms are held to carbon atoms. The C-C bonds have a length of 1.54A, as against 1.10A for the C-H bonds, and they serve different purposes insofar as their contribution to the strength of the crystals is concerned. The strength of a polyethylene chain depends entirely on the strength and degrees of freedom of the C-C bond. On the other hand, because of its geometric and steric configuration, the C-H bond plays an important role in determining the crystal structure and providing the intermolecular electrokinetic forces to be discussed later.

In a polyethylene molecule all four valencies of carbon are satisfied and its four bonds are directed in space as shown in Figure 1.3. In general, segments of this molecule are free to rotate about the C-C bond in such a manner that any three carbon atoms always form a plane. However, as described in Section 1.3, the molecular chains take up a planar zigzag conformation in polyethylene single crystals and thereby prevent any rotation about the C-C bond.

has be

for the

The fo

chain a

the ab

molec

stretc

be ma

consta

ii) In

is suc

The a

in the

secor

becar

carb

attra

mom

diffe

Thes

them

due t

The strength of C-C bonds for various types of deformation has been determined by Mizushima and Shimanouchi (15), and values for these and other geometric parameters are listed in Section 2.5. The force between two alternate chemical units of $-CH_2-$ along the chain axis is repulsive due to their being too near each other. In the absence of any free rotation about the C-C bond, deformation of molecular chains will take place by a process of deformation involving stretching, bending and repulsive force constants only. This fact will be made use of later in Section 2.4, to obtain the interaction force constants.

ii) Intermolecular Forces

As discussed in Section 1.3, the crystal lattice of polyethylene is such that adjacent molecular chains occupy an orthorhombic cell. The attractive forces between these chains, which bind them together in the solid crystalline form, are called the intermolecular or secondary valence forces.

Polyethylene is a nonpolar material for two reasons. First, because all the valencies are satisfied and, second, because both carbon and hydrogen are equally electronegative. Therefore, the attractive intermolecular force is not due to permanent dipole moments, but rather to time varying dipole moments resulting from different instantaneous configurations of the electrons and nuclei. These are also called London dispersion forces; the potential governing them is proportional to the inverse sixth power of the distance (20).

Between any two molecules, there is also a repulsive force due to the interference of the electron clouds surrounding the nuclei.

This force is short-range compared to the London attractive force, decreasing exponentially with distance (21, 22, 23).

At the equilibrium separation the net force is zero; and, of course, the net energy, or the potential curve, will have a minimum at this distance.

Different portions of the exponentially-decreasing repulsive potential function may, for convenience, be matched by different inverse powers of the distance (24, 25). If for polyethylene, as suggested by Geil (6), we approximate this potential by the twelfth power, the total potential energy function ϕ may be written as

$$\phi(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} , \qquad 2.26$$

where r represents the separation distance and A and B are constants called the Lennard-Jones potential constants. This is the standard form of the Lennard-Jones 6-12 potential (26).

Evaluation of A and B the Lennard-Jones Constants

The shape of the general potential curve $\phi(r)$ is as shown below:

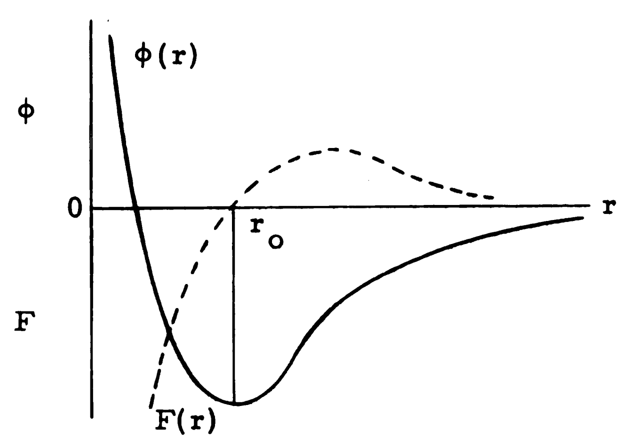


Figure 2.3. Lennard-Jones 6-12 potential curve $\phi(r)$ and force curve $F(r)$.

The gra

molecu

or

The cu

r_0 im

defini

gives

or

The gradient of $\phi(r)$ will give the force $F(r)$ between two adjacent molecules. Thus, we may write

$$F(r) = -\frac{d\phi(r)}{dr} \qquad 2.27$$

or

$$F(r) = \frac{12A}{r^{13}} - \frac{6B}{r^{7}} \; . \qquad 2.28$$

The curve of $F(r)$ is also shown in Figure 2.3.

The force $F(r)$ being zero at the known equilibrium distance r_o imposes the condition that the constants A and B have a certain definite ratio;

$$F(r) = 0 \qquad 2.29$$

gives

$$\frac{12A}{r_o^{13}} - \frac{6B}{r_o^{7}} = 0 \qquad 2.30$$

or

$$\frac{1}{r_o^7}\left(\frac{12A}{r_o^6} - 6\,B\right) = 0 \; ,$$

$$\frac{12A}{r_o^6} - 6\,B = 0$$

$$\frac{A}{B} = \frac{6}{12}\; r_o^6$$

$$\frac{A}{B} = \frac{1}{2}\; r_o^6 \; . \qquad 2.31a$$

Rewrit

where

and su

obtain

which

crysta

Lemma

cohes

The c

the e

occup

It is

in a r

U, is

and is

units,

with

lattice

by Δ

Rewriting 2.31a as

$$A = p\,B \;, \qquad 2.31b$$

where $p = \frac{1}{2}\, r_o^6$ is a known constant, 2.32

and substituting for A in terms of B from 2.31b in 2.26, we obtain the potential $\phi(r)$ in the form

$$\phi(r) = \frac{pB}{r^{12}} - \frac{B}{r^6} \;, \qquad 2.33$$

which involves only one unknown constant.

The constant B can now be determined by computing the crystal potential energy density, in a manner similar to that used by Lennard-Jones (26) for cubic crystals, and by comparing it with the cohesive energy density—an experimentally-determined value (16). The crystal potential energy density, denoted by E, is defined as the energy per mole of polyethylene, in which the individual units occupying the lattice points are surrounded by an infinite matrix. It is computed by summing the lattice energy of the individual units in a mole of the crystal. The lattice energy of a unit, , denoted by U, is the energy of the unit when in the lattice of an infinite crystal and is the sum of the contributions $\phi(r)$, due to all surrounding units, where

$$\phi(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$$

with r the distance of the surrounding units from the unit whose lattice energy is being calculated. Cohesive energy density, denoted by Δ , is the energy per mole of a substance that is required to remove a unit from the matrix to a postion far from its neighbors.

Evalu

will c

$\cdot C_2$

conn

Secti

show

(0,

(0,

(0,

(0,

I

Lett

and

Evaluation of Lattice Energy and Crystal Potential Energy Density

For purposes of evaluating the crystal potential energy, we will consider polyethylene single crystals to be made up of units of $(-C_2H_4-)$ (Figure 2.2). This model will also be used later in connection with the development of interaction force constants in Section 2.3. The lattice structure may, thus, be represented as shown below:

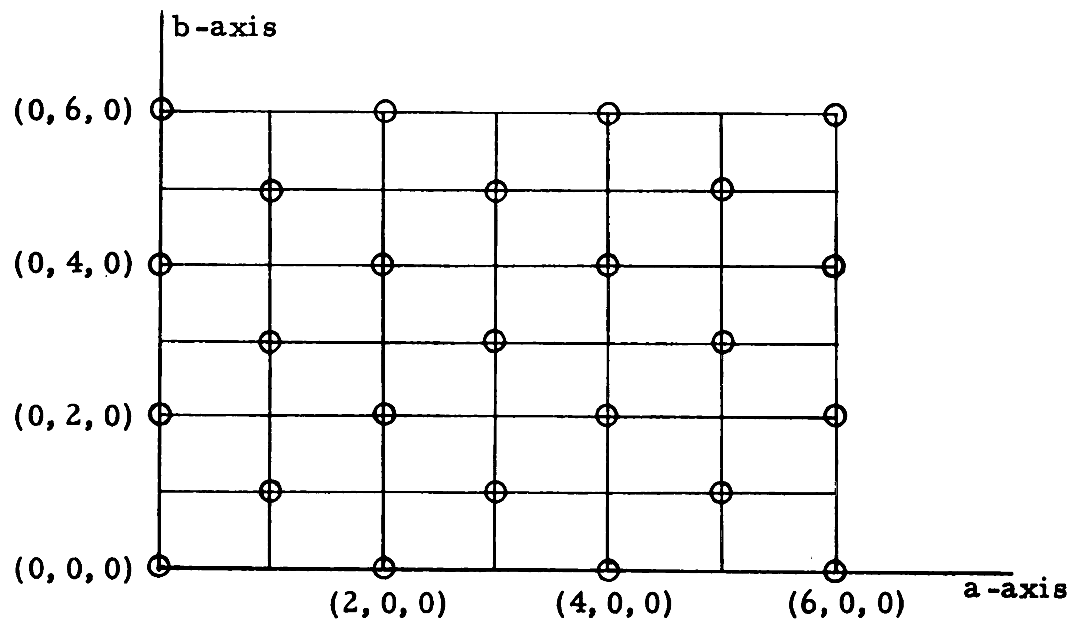


Figure 2.4. Schematic representation of two-dimensional lattice structure with lattice points occupied by $(-C_2H_4-)$ units.

Letting

$$a/2 = e_1$$
$$b/2 = e_2 \qquad 2.34$$

and

$$c = e_3 .$$

we may

where

the a,

is

From

even (

units

belon

throu

that v

wher

we may then write the position vector of a lattice point (ℓ, m, n) as

$$\vec{r}_{\ell mn} = \ell e_1 \hat{i}_1 + m e_2 \hat{i}_2 + n e_3 \hat{i}_3 \quad , \qquad 2.35$$

where ℓ, m, n are integers and $\hat{i}_1$, $\hat{i}_2$, $\hat{i}_3$ are unit vectors along the a, b and c axes respectively. Therefore, the distance $r_{\ell mn}$ is

$$r_{\ell mn} = [(\ell e_1)^2 + (m e_2)^2 + (n e_3)^2]^{1/2} \ . \qquad 2.36$$

From Figure 2.4 it can be seen that only when ℓ and m are both even or both odd is the point occupied by a real unit. Also, all the units for which both ℓ and m are zero should be excluded; they belong to a single chain and, hence, are permanently attached through the C-C bonds.

It follows from 2.26, which gives the energy of a pair of units, that we can calculate the lattice energy U of a (0, 0, 0) unit from

$$U = \frac{1}{2} \sum_{\ell, m, n=-\infty}^{\infty} \phi_{\ell mn}(r) \qquad 2.37$$

$$= \frac{1}{2} \Sigma \left(\frac{A}{r_{\ell mn}^{12}} - \frac{B}{r_{\ell mn}^{6}} \right) \qquad 2.38$$

$$= \frac{1}{2} \left[\Sigma \left(\frac{p}{r_{\ell mn}^{12}} - \frac{1}{r_{\ell mn}^{6}} \right) \right] B \ , \qquad 2.39$$

where from 2.32

$$p = \frac{1}{2} (r_o)^6 \ ,$$

and both ℓ and m are odd or even and n equals any integer, but ℓ, m, n $\neq$ 0.

This reduces the problem to one of calculating sums of the type

$$A_s = \sum_{\ell, m, n=-\infty}^{\infty} \frac{1}{r_{\ell mn}^{s}} \qquad 2.40$$

for s = 12 or 6.

Substituting for

$$r_{\ell mn}^2 = (\ell e_1)^2 + (me_2)^2 + (ne_3)^2$$

from 2.36, we get

$$A_s = \sum_{\ell, m, n=-\infty}^{\infty} \frac{1}{[(\ell e_1)^2 + (me_2)^2 + (ne_3)^2]^{s/2}} \qquad 2.41$$

Therefore we may write U in the form

$$U = \frac{1}{2} B\,(p\,A_{12} - A_6) \qquad 2.42$$

$$= \frac{1}{2} B\,A_{12\text{-}6} \qquad 2.43$$

where $A_{12\text{-}6} = p\,A_{12} - A_6$.

<u>Crystal Potential Energy and Cohesive Energy</u>

A gram mole of a substance contains 6.0249×10^{23} units, called Avogadro's number and denoted by N_A . Let M be the molecular weight of the lattice units ($-C_2H_4-$). Therefore, M grams of polyethylene will contain N_A units. Thus, the crystal potential energy per mole E is

$$E = N_A U , \tag{2.44}$$

where U is the lattice energy of a single unit, as determined in 2.43.

The cohesive energy density has been determined by Small (16). However, he gives values of δ, which is the square root of the cohesive energy per unit volume; thus, δ^2 determines the cohesive energy per unit volume. In order to convert this to a molar value we must determine the volume of a mole of crystalline polyethylene. If ρ is the density of such material, the volume V of M grams will be

$$V = \frac{M}{\rho} . \tag{2.45}$$

Therefore, the cohesive energy per mole, Δ, is

$$\Delta = \frac{M}{\rho} \delta^2 ; \tag{2.46}$$

and equating the values of Δ and E obtained in 2.46 and 2.44, we arrive at:

$$\Delta = E \tag{2.47}$$

$$\frac{M}{\rho} \delta^2 = N_A U \tag{2.48}$$

But from 2.43

$$U = \frac{1}{2} B A_{12-6} ,$$

which when substituted in 2.48 gives

The

by ex

in Se

const

serie

2.3.

con

cor

mo

va

s

m

cor

and

poten

the inter

$$B = \frac{2 M \delta^2}{N_A \rho A_{12\text{-}6}} \quad . \qquad 2.49$$

The expression for A then follows from 2.31b:

$$A = p B$$

$$= \frac{2 p M \delta^2}{N_A \rho A_{12\text{-}6}} \qquad 2.50$$

The Lennard-Jones potential constants A and B, defined by expressions 2.49 and 2.50 will be evaluated numerically later in Section 2.5, by substitution of the values of several physical constants such as M, N_A, ρ and p, and by making use of the series summation for $A_{12\text{-}6}$ developed in Appendix I.

2.3. Interaction Constants and Elastic Constants

In order to calculate continuum or macroscopic elastic constants in terms of molecular force constants, it is necessary to consider the forces of interaction that result when a lattice unit moves relative to the units which surround it. Since the force fields vary nearly linearly with distance for small displacements, the slopes of the force curves at the separation distances of the surrounding units determine the so-called interaction constants. These constants may, therefore, be obtained in terms of the intramolecular force constants (such as the C-C bond stretching or contraction, bending and repulsive force constants) and the intermolecular Lennard-Jones potential constants.

In this section a connection between the elastic constants and the interaction constants of polyethylene single crystals is established

by following a procedure similar to von Kármán's for simple cubic crystals, as discussed in Reference (14) by Kittel. Components of the net force acting on a unit are obtained by considering its interactions with the surrounding units up to second nearest-neighbors. These expressions, which involve finite displacements, are converted into partial differential equations by introducing the lattice parameters a, b and c, and by taking limits. Newton's law is then applied to convert the force equations into equations of motion, in order to compare these with the corresponding continuum Equations 2.25.

A comparison of the coefficients of appropriate partial derivatives in the two sets of equations yields the desired expressions for the elastic constants in terms of the interaction constants. These expressions may be modified to apply to first nearest-neighbor interactions only simply by eliminating the terms pertaining to second nearest-neighbors. Also, the central force assumption is applied in a rather limited manner to polyethylene single crystals. The C-C bonds along the chain axis have strong resistance to bending in directions normal to the chain and, thus, make the forces between units on the same chain non-central. The forces between units on different chains may, however, be treated as central.

Model and Notation

Consider again, as in Section 2.2, that the lattice points are occupied by ($-C_2H_4-$) units. Figures 2.5 and 2.6 show both the first and the second nearest-neighbors in one quadrant formed by the positive x, y and z-axes. An additional axis (x') along the diagonal of the rectangle (a, b) in the xy-plane is also shown.

Fi

Fi

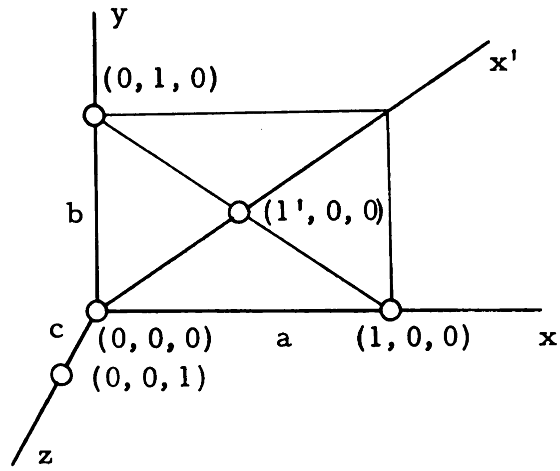


Figure 2.5. First nearest-neighbors in the first quadrant only.

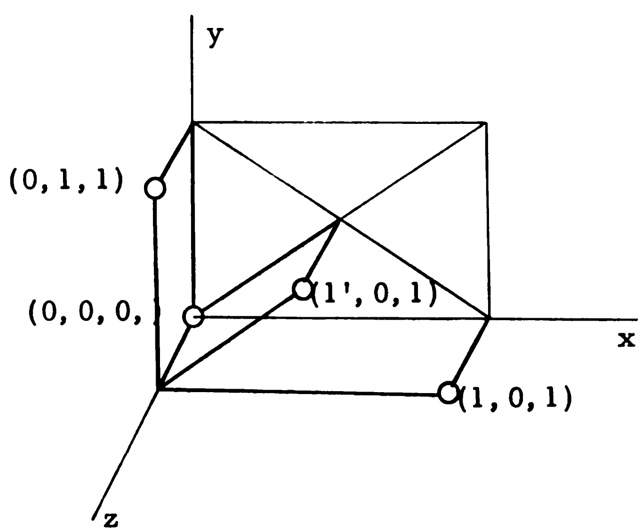


Figure 2.6. Second nearest-neighbors in the first quadrant only.

Figur

I

Sim

l-a,

F

If y' is considered to be in the xy-plane, normal to x', Figure 2.7 then represents the $x'y'z$ set of axes.

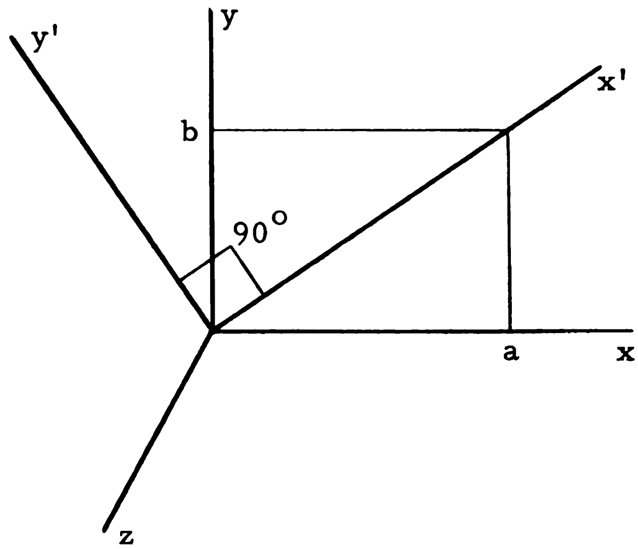


Figure 2.7. Rotation of x' y' z with respect to x y z.

Similarly, by considering x'' to be along the diagonal of the rectangle $(-a, b)$, the $x''y''z$ set of axes is shown in Figure 2.8.

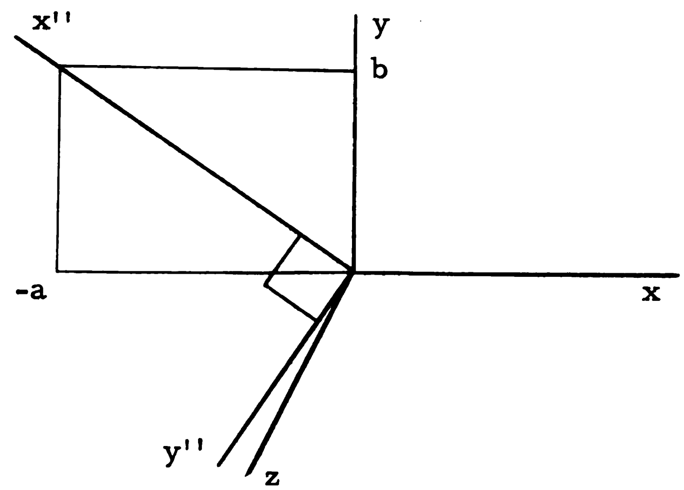


Figure 2.8. Rotation of x'' y'' z with respect to x y z.

along

be la

Thus

(1,

Only

It m

equ

of th

are

ethy

(1'',

be f

(

(

are

how

firs

to (

(1'',

Equ

unt

Considering a, b, c and $\frac{1}{2}\sqrt{a^2 + b^2}$ as units of distances along the respective axes x, y, z, x' and x'', the lattice points may be labelled by their (ℓ, m, n) coordinates, ℓ, m and n being integers. Thus, the points listed below indicate first nearest-neighbors:

$$(1, 0, 0), (-1, 0, 0); (0, 1, 0), (0, -1, 0); (0, 0, 1), (0, 0, -1); (1', 0, 0), (-1', 0, 0)$$
$$\text{and } (1'', 0, 0), (-1'', 0, 0) \qquad 2.51$$

Only four of the first ten nearest-neighbors are shown in Figure 2.5. It may be observed that nearest-neighbors, as defined here, are not equidistant from the central unit (0, 0, 0). This is due to the geometry of the orthorhombic cell, for which the three parameters a, b and c are inherently unequal. An additional feature peculiar to the polyethylene lattice structure is that units corresponding to (1', 0, 0) and (1'', 0, 0), along the x' and x''-axes respectively, are considered to be first nearest-neighbors.

Similarly, the points

$$(0, 1, 1), (0, -1, 1), (0, 1, -1), (0, -1, -1); (1, 0, 1), (-1, 0, 1), (1, 0, -1), (-1, 0, -1);$$
$$(1', 0, 1), (-1', 0, 1), (1', 0, -1), (-1', 0, -1) \text{ and } (1'', 0, 1), (-1'', 0, 1),$$
$$(1'', 0, -1), (-1'', 0, -1) \qquad 2.52$$

are the second nearest-neighbors. These are sixteen in number; however, only three are shown in Figure 2.6, in addition to the four first nearest-neighbors. It should be noted that the units corresponding to (1, 1, 0) are excluded because units corresponding to (1', 0, 0) and (1'', 0, 0) lie between these and the central unit (0, 0, 0).

Equations of Motion

Let F_x, F_y and F_z be the components of the force on the unit (0, 0,0) along the axes x, y and z, respectively. Similarly, the

displacement components of the unit at (ℓ, m, n) may be represented by $u_{\ell mn}$, $v_{\ell mn}$ and $w_{\ell mn}$. Interaction constants will be different for different units and will also depend upon the direction of the displacement. Defining $k^{ij}_{\ell mn}$ as the force on the unit (0, 0, 0) along the x_i-axis per unit displacement u_j of the unit (ℓ, m, n), where $i, j = 1, 2, 3$ and x_1, x_2, x_3 correspond to x, y and z while u_1, u_2 and u_3 correspond to u, v and w, respectively, the interaction force components F_x, F_y and F_z are derived below:

$$
\begin{aligned}
F_x = {} & k^{11}_{100}(u_{100} + u_{-100} - 2u_{000}) + k^{11}_{010}(u_{010} + u_{0-10} - 2u_{000}) \\
& + k^{11}_{001}(u_{001} + u_{00-1} - 2u_{000}) + k^{11}_{1'00}[(u_{1'00} + u_{-1'00} - 2u_{000}) \\
& + (u_{1''00} + u_{-1''00} - 2u_{000})] + k^{11}_{101}[(u_{101} + u_{-10-1} - 2u_{000}) \\
& + (u_{-101} + u_{10-1} - 2u_{000})] + k^{13}_{101}[(w_{101} + w_{-10-1} - 2w_{000}) \\
& - (w_{-101} + w_{10-1} - 2w_{000})] + k^{11}_{011}[(u_{011} + u_{0-1-1} - 2u_{000}) \\
& + (u_{01-1} + u_{0-11} - 2u_{000})] \qquad\qquad 2.53 \\
& + k^{11}_{1'01}\{[(u_{1'01} + u_{-1'0-1} - 2u_{000}) + (u_{-1'01} + u_{1'0-1} - 2u_{000})] \\
& + [(u_{1''01} + u_{-1''0-1} - 2u_{000}) + (u_{-1''01} + u_{1''0-1} - 2u_{000})]\} \\
& + k^{13}_{1'01}\{[(w_{1'01} + w_{-1'0-1} - 2w_{000}) - (w_{-1'01} + w_{-1'0-1} - 2w_{000})] \\
& + [(w_{1''01} + w_{-1''0-1} - 2w_{000}) - (w_{-1''01} + w_{1''0-1} - 2w_{000})]\} \\
& + k^{12}_{1'01}\{[(v_{1'01} + v_{-1'0-1} - 2v_{000}) - (v_{-1'01} + v_{-1'0-1} - 2v_{000})] \\
& + [(v_{1''01} + v_{-1''0-1} - 2v_{000}) - (v_{-1''01} + v_{1''0-1} - 2v_{000})]\} .
\end{aligned}
$$

Expr

may

$F_x =$

$+$

$+$

$+$

whic

k

$F_y =$

$+$

$+$

$+$

whic

k

Expressing $(u_{\ell mn} + u_{-\ell -m-n} - 2u_{000})$, for example, as $(\bar{u}_{\ell mn})$, we may rewrite 2.53 in the form

$$
\begin{aligned}
F_x = {} & k^{11}_{100}(\bar{u}_{100}) + k^{11}_{010}(\bar{u}_{010}) + k^{11}_{001}(\bar{u}_{001}) \\
& + k^{11}_{1'00}[(\bar{u}_{1'00}) + (\bar{u}_{1''00})] + k^{11}_{101}[(\bar{u}_{101}) + (\bar{u}_{-101})] \\
& \qquad + k^{13}_{101}[(\bar{w}_{101}) - (\bar{w}_{-101})] + k^{11}_{011}[(\bar{u}_{011}) + (\bar{u}_{01-1})] \\
& + k^{11}_{1'01}\{[(\bar{u}_{1'01}) + (\bar{u}_{-1'01})] + [(\bar{u}_{1''01}) + (\bar{u}_{-1''01})]\} \\
& \qquad + k^{13}_{1'01}\{[(\bar{w}_{1'01}) - (\bar{w}_{-1'01})] + [(\bar{w}_{1''01}) - (\bar{w}_{-1''01})]\} \\
& + k^{12}_{1'01}\{[(\bar{v}_{1'01}) - (\bar{v}_{-1'01})] + [(\bar{v}_{1''01}) - (\bar{v}_{-1''01})]\} \;.
\end{aligned} \tag{2.54}
$$

which involves the following ten interaction constants:

$$k^{11}_{100},\ k^{11}_{010},\ k^{11}_{001},\ k^{11}_{1'00},\ k^{11}_{101},\ k^{13}_{101},\ k^{11}_{011},\ k^{11}_{1'01},\ k^{13}_{1'01} \text{ and } k^{12}_{1'01} \tag{2,55}$$

The component of force F_y may be written as

$$
\begin{aligned}
F_y = {} & k^{22}_{100}(\bar{v}_{100}) + k^{22}_{010}(\bar{v}_{010}) + k^{22}_{001}(\bar{v}_{001}) \\
& + k^{22}_{1'00}[(\bar{v}_{1'00}) + (\bar{v}_{1''00})] + k^{22}_{011}[(\bar{v}_{011}) + (\bar{v}_{01-1})] \\
& \qquad + k^{23}_{011}[(\bar{w}_{011}) - (\bar{w}_{01-1})] \\
& + k^{22}_{1'01}\{[(\bar{v}_{1'01}) + (\bar{v}_{-1'01})] + [(\bar{v}_{1''01}) + (\bar{v}_{-1''01})]\} \\
& \qquad + k^{21}_{1'01}\{[(\bar{u}_{1'01}) - (\bar{u}_{-1'01})] + [(\bar{u}_{1''01}) - (\bar{u}_{-1''01})]\} \\
& + k^{23}_{1'01}\{[(\bar{w}_{1'01}) - (\bar{w}_{-1'01})] + [(\bar{w}_{1''01}) - (\bar{w}_{-1''01})] \;,
\end{aligned} \tag{2.56}
$$

which involves the nine following interaction constants:

$$k^{22}_{100},\ k^{22}_{010},\ k^{22}_{001},\ k^{22}_{1'00},\ k^{22}_{011},\ k^{23}_{011},\ k^{22}_{1'01},\ k^{21}_{1'01} \text{ and } k^{23}_{1'01} \tag{2.57}$$

And, similarly, the component of force F_z is

$$
\begin{aligned}
F_z = {} & k^{33}_{100}(\overline{w}_{100}) + k^{33}_{010}(\overline{w}_{010}) + k^{33}_{001}(\overline{w}_{001}) \\
& + k^{33}_{1'00}[(\overline{w}_{1'00}) + (\overline{w}_{1''00})] + k^{33}_{101}[(\overline{w}_{101}) + (\overline{w}_{-101})] \\
& \quad + k^{31}_{101}[(\overline{u}_{101}) - (\overline{u}_{-101})] + k^{33}_{011}[(\overline{w}_{011}) + (\overline{w}_{01-1})] \\
& \quad + k^{32}_{011}[(\overline{v}_{011}) - (\overline{v}_{01-1})] \\
& + k^{33}_{1'01}\{[(\overline{w}_{1'01}) + (\overline{w}_{-1'01})] + [(\overline{w}_{1''01}) + (\overline{w}_{-1''01})]\} \\
& \quad + k^{32}_{1'01}\{[(\overline{v}_{1'01}) - (\overline{v}_{-1'0-1})] + [(\overline{v}_{1''01}) - (\overline{v}_{-1''01})]\} \\
& + k^{31}_{1'01}\{[(\overline{u}_{1'01}) - (\overline{u}_{-1'01})] + [(\overline{u}_{1''01}) - (\overline{u}_{-1''01})]\} , \qquad 2.58
\end{aligned}
$$

involving the eleven following interaction constants:

$$
\begin{aligned}
& k^{33}_{100},\ k^{33}_{010},\ k^{33}_{001},\ k^{33}_{1'00},\ k^{33}_{101},\ k^{31}_{101},\ k^{33}_{011},\ k^{32}_{011},\ k^{33}_{1'01}, \\
& \qquad k^{32}_{1'01} \text{ and } k^{31}_{1'01} \qquad 2.59
\end{aligned}
$$

Thus, the total number of interaction constants involved in all three force equations is $10+9+11 = 30$.

Dividing through by the respective lattice distances and taking limits, the above difference equations 2.53-59 can be converted into the partial differential equations given below:

$$
\begin{aligned}
F_x = {} & k^{11}_{100}\, a^2 \frac{\partial^2 u}{\partial x^2} + k^{11}_{010}\, b^2 \frac{\partial^2 u}{\partial y^2} + k^{11}_{001}\, c^2 \frac{\partial^2 u}{\partial z^2} + k^{11}_{1'00} \frac{a^2+b^2}{4} \\
& \left(\frac{\partial^2 u}{\partial x_{12}^2} + \frac{\partial^2 u}{\partial x_{21}^2}\right) + k^{11}_{101}\,(a^2 + c^2)\left(\frac{\partial^2 u}{\partial x_{13}^2} + \frac{\partial^2 u}{\partial x_{31}^2}\right)
\end{aligned}
$$

$$+ k_{101}^{13}\,(a^2+c^2)\left(\frac{\partial^2 w}{\partial x_{13}^2} - \frac{\partial^2 w}{\partial x_{31}^2}\right) + k_{011}^{11}\,(b^2+c^2)\left(\frac{\partial^2 u}{\partial x_{23}^2} + \frac{\partial^2 u}{\partial x_{32}^2}\right)$$

$$+ k_{1'01}^{11}\,\left(\frac{a^2+b^2+4c^2}{4}\right)\left[\left(\frac{\partial^2 u}{\partial x_{1'3}^2} + \frac{\partial^2 u}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 u}{\partial x_{1''3}^2} + \frac{\partial^2 u}{\partial x_{31''}^2}\right)\right]$$

$$+ k_{1'01}^{13}\,\left(\frac{a^2+b^2+4c^2}{4}\right)\left[\left(\frac{\partial^2 w}{\partial x_{1'3}^2} - \frac{\partial^2 w}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 w}{\partial x_{1''3}^2} - \frac{\partial^2 w}{\partial x_{31''}^2}\right)\right]$$

$$+ k_{1'01}^{12}\,\left(\frac{a^2+b^2+4c^2}{4}\right)\left[\left(\frac{\partial^2 v}{\partial x_{1'3}^2} - \frac{\partial^2 v}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 v}{\partial x_{1''3}^2} - \frac{\partial^2 v}{\partial x_{31''}^2}\right)\right] \qquad 2.60$$

$$F_y = k_{100}^{22}\,a^2\,\frac{\partial^2 v}{\partial x^2} + k_{010}^{22}\,b^2\,\frac{\partial^2 v}{\partial y^2} + k_{001}^{22}\,c^2\,\frac{\partial^2 v}{\partial z^2}$$

$$+ k_{100}^{22}\,\left(\frac{a^2+b^2}{4}\right)\left(\frac{\partial^2 v}{\partial x_{12}^2} + \frac{\partial^2 v}{\partial x_{21}^2}\right) + k_{011}^{22}\,(b^2+c^2)\left(\frac{\partial^2 v}{\partial x_{23}^2} + \frac{\partial^2 v}{\partial x_{32}^2}\right)$$

$$+ k_{011}^{23}\,(b^2+c^2)\left(\frac{\partial^2 w}{\partial x_{23}^2} - \frac{\partial^2 w}{\partial x_{32}^2}\right)$$

$$+ k_{1'01}^{22}\,\left(\frac{a^2+b^2+4c^2}{4}\right)\left[\left(\frac{\partial^2 v}{\partial x_{1'3}^2} + \frac{\partial^2 v}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 v}{\partial x_{1''3}^2} + \frac{\partial^2 v}{\partial x_{31''}^2}\right)\right]$$

$$+ k_{1'01}^{21}\,\left(\frac{a^2+b^2+4c^2}{4}\right)\left[\left(\frac{\partial^2 u}{\partial x_{1'3}^2} - \frac{\partial^2 u}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 u}{\partial x_{1''3}^2} - \frac{\partial^2 u}{\partial x_{31''}^2}\right)\right]$$

$$+ k_{1'01}^{23}\,\left(\frac{a^2+b^2+4c^2}{4}\right)\left[\left(\frac{\partial^2 w}{\partial x_{1'3}^2} - \frac{\partial^2 w}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 w}{\partial x_{1''3}^2} - \frac{\partial^2 w}{\partial x_{31''}^2}\right)\right] \qquad 2.61$$

$$F_z = k^{33}_{100}\, a^2 \frac{\partial^2 w}{\partial x^2} + k^{33}_{010}\, b^2 \frac{\partial^2 w}{\partial y^2} + k^{33}_{001}\, c^2 \frac{\partial^2 w}{\partial z^2}$$

$$+ k^{33}_{1'00}\left(\frac{a^2+b^2}{4}\right)\left(\frac{\partial^2 w}{\partial x_{12}^2} + \frac{\partial^2 w}{\partial x_{21}^2}\right) + k^{33}_{101}\,(a^2+c^2)\left(\frac{\partial^2 w}{\partial x_{13}^2} + \frac{\partial^2 w}{\partial x_{31}^2}\right)$$

$$+ k^{31}_{101}\,(a^2+c^2)\left(\frac{\partial^2 u}{\partial x_{13}^2} - \frac{\partial^2 u}{\partial x_{31}^2}\right) + k^{33}_{011}\,(b^2+c^2)\left(\frac{\partial^2 w}{\partial x_{23}^2} + \frac{\partial^2 w}{\partial x_{32}^2}\right)$$

$$+ k^{32}_{011}\,(b^2+c^2)\left(\frac{\partial^2 v}{\partial x_{23}^2} - \frac{\partial^2 v}{\partial x_{32}^2}\right)$$

$$+ k^{33}_{1'01}\left(\frac{a^2+b^2+4c^2}{4}\right)\left[\left(\frac{\partial^2 w}{\partial x_{1'3}^2} + \frac{\partial^2 w}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 w}{\partial x_{1''3}^2} + \frac{\partial^2 w}{\partial x_{31''}^2}\right)\right]$$

$$+ k^{31}_{1'01}\left[\left(\frac{\partial^2 u}{\partial x_{1'3}^2} - \frac{\partial^2 u}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 u}{\partial x_{1''3}^2} - \frac{\partial^2 u}{\partial x_{31''}^2}\right)\right]$$

$$+ k^{32}_{1'01}\left[\left(\frac{\partial^2 v}{\partial x_{1'3}^2} - \frac{\partial^2 v}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 v}{\partial x_{1''3}^2} - \frac{\partial^2 v}{\partial x_{31''}^2}\right)\right] \qquad 2.62$$

Here, the x_{ij} diagonal axes lie in the $x_i x_j$-plane, where $i, j = 1, 2, 3, 1'$ and $1''$, such that $x_{1'3}$ is the diagonal axis along the rectangle $(\frac{1}{2}\sqrt{a^2 + b^2},\ c)$ in the $x'z$-plane. These axes are shown in Figure 2.9 a-e below:

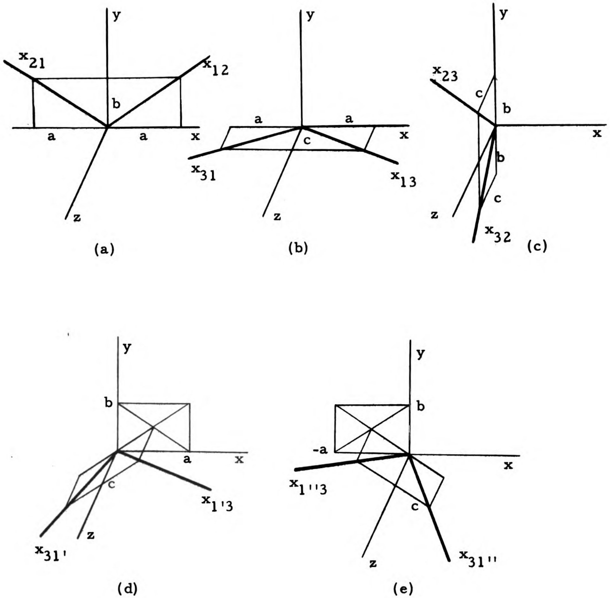


Figure 2.9. Geometrical representation of axes x_{ij}
(a) x_{12} and x_{21} (b) x_{13} and x_{31} (c) x_{23} and x_{32}
(d) $x_{1'3}$ and $x_{31'}$ (e) $x_{1''3}$ and $x_{31''}$.

Transforming partial derivatives with respect to the x_{ij}'s into partial derivatives with respect to x, y and z in Equations 2.60-62, by utilizing the transformations derived in Appendix II, these equations become:

$$F_x = k^{11}_{100}\, a^2 \frac{\partial^2 u}{\partial x^2} + k^{11}_{010}\, b^2 \frac{\partial^2 u}{\partial y^2} + k^{11}_{001}\, c^2 \frac{\partial^2 u}{\partial z^2}$$

$$+ \frac{1}{2} k^{11}_{1'00} \left(a^2 \frac{\partial^2 u}{\partial x^2} + b^2 \frac{\partial^2 u}{\partial y^2} \right) + 2\, k^{11}_{101} \left(a^2 \frac{\partial^2 u}{\partial x^2} + c^2 \frac{\partial^2 u}{\partial z^2} \right)$$

$$+ k^{13}_{101}\, ac \frac{\partial^2 w}{\partial x \partial z} + 2\, k^{11}_{011} \left(b^2 \frac{\partial^2 u}{\partial y^2} + c^2 \frac{\partial^2 u}{\partial z^2} \right)$$

$$+ k^{11}_{1'01} \left(a^2 \frac{\partial^2 u}{\partial x^2} + b^2 \frac{\partial^2 u}{\partial y^2} + 4c^2 \frac{\partial^2 u}{\partial z^2} \right)$$

$$+ 4k^{13}_{1'01}\, bc \frac{\partial^2 w}{\partial x \partial z} + 4\, k^{12}_{101}\, bc \frac{\partial^2 w}{\partial y \partial z} \qquad 2.63$$

$$F_y = k^{22}_{100}\, a^2 \frac{\partial^2 v}{\partial x^2} + k^{22}_{010}\, b^2 \frac{\partial^2 v}{\partial y^2} + k^{22}_{001}\, c^2 \frac{\partial^2 v}{\partial z^2}$$

$$+ \frac{1}{2} k^{22}_{1'00} \left(a^2 \frac{\partial^2 v}{\partial x^2} + b^2 \frac{\partial^2 v}{\partial y^2} \right) + 2k^{22}_{011} \left(b^2 \frac{\partial^2 v}{\partial y^2} + c^2 \frac{\partial^2 v}{\partial z^2} \right)$$

$$+ 4k^{23}_{011}\, bc \frac{\partial^2 w}{\partial y \partial z} + k^{22}_{1'01} \left(a^2 \frac{\partial^2 v}{\partial x^2} + b^2 \frac{\partial^2 v}{\partial y^2} + 4c^2 \frac{\partial^2 v}{\partial z^2} \right)$$

$$+ 4k^{21}_{1'01}\, bc \frac{\partial^2 u}{\partial y \partial z} + 4k^{23}_{1'01}\, bc \frac{\partial^2 w}{\partial y \partial z} \qquad 2.64$$

$$F_z = k^{33}_{100}\, a^2 \frac{\partial^2 w}{\partial x^2} + k^{33}_{010}\, b^2 \frac{\partial^2 w}{\partial y^2} + k^{33}_{001}\, c^2 \frac{\partial^2 w}{\partial z^2}$$

$$+ \frac{1}{2}\, k^{33}_{1'00} \left(a^2 \frac{\partial^2 w}{\partial x^2} + b^2 \frac{\partial^2 w}{\partial y^2}\right) + 2\, k^{33}_{101} \left(a^2 \frac{\partial^2 w}{\partial x^2} + c^2 \frac{\partial^2 w}{\partial z^2}\right)$$

$$+ 4k^{31}_{101}\, ac \frac{\partial^2 u}{\partial x \partial z} + 2k^{33}_{011} \left(b^2 \frac{\partial^2 w}{\partial y^2} + c^2 \frac{\partial^2 w}{\partial z^2}\right) + 4k^{32}_{011}\, bc \frac{\partial^2 v}{\partial y \partial z}$$

$$+ k^{33}_{1'01} \left(a^2 \frac{\partial^2 w}{\partial x^2} + b^2 \frac{\partial^2 w}{\partial y^2} + 4c^2 \frac{\partial^2 w}{\partial z^2}\right) + 4k^{31}_{1'01}\, bc \frac{\partial^2 u}{\partial y \partial z}$$

$$+ 4k^{32}_{1'01}\, bc \frac{\partial^2 v}{\partial y \partial z} \qquad 2.65$$

By collecting coefficients of the various partial derivatives, the above equations may be rewritten as:

$$F_x = a^2(k^{11}_{100} + \frac{1}{2} k^{11}_{1'00} + 2\, k^{11}_{101} + k^{11}_{1'01}) \frac{\partial^2 u}{\partial x^2} + b^2(k^{11}_{010} + \frac{1}{2} k^{11}_{1'00} + 2k^{11}_{011}$$

$$+ k^{11}_{1'01}) \frac{\partial^2 u}{\partial y^2} + c^2 (k^{11}_{001} + 2k^{11}_{101} + 2k^{11}_{011} + 4k^{11}_{1'01}) \frac{\partial^2 u}{\partial z^2} + 4\, a\, c\, k^{13}_{101} \frac{\partial^2 w}{\partial x \partial z}$$

$$+ 4\, b\, c\, k^{13}_{1'01} \frac{\partial^2 w}{\partial y \partial z} + 4\, b\, c\, k^{12}_{1'01} \frac{\partial^2 v}{\partial y \partial z} \qquad 2.66$$

$$F_y = a^2(k^{22}_{100} + \frac{1}{2} k^{22}_{1'00} + k^{22}_{1'01}) \frac{\partial^2 v}{\partial x^2} + b^2 (k^{22}_{010} + \frac{1}{2} k^{22}_{1'00} + 2k^{22}_{011} + k^{22}_{1'01}) \frac{\partial^2 v}{\partial y^2}$$

$$+ c^2 (k^{22}_{001} + 2k^{22}_{011} + 4k^{22}_{1'01}) \frac{\partial^2 v}{\partial z^2} + 4\, b\, c(k^{23}_{011} + k^{23}_{1'01}) \frac{\partial^2 w}{\partial y \partial z}$$

$$+ 4\, b\, c\, k^{21}_{1'01} \frac{\partial^2 u}{\partial y \partial z} \qquad 2.67$$

$$F_z = a^2 \left(k^{33}_{100} + \frac{1}{2} k^{33}_{1'00} + 2 k^{33}_{101} + k^{33}_{1'01}\right) \frac{\partial^2 w}{\partial x^2}$$

$$+ b^2 \left(k^{33}_{010} + \frac{1}{2} k^{33}_{1'00} + 2 k^{33}_{011} + k^{33}_{1'01}\right) \frac{\partial^2 w}{\partial y^2}$$

$$+ c^2 \left(k^{33}_{001} + 2 k^{33}_{101} + 2 k^{33}_{011} + 4 k^{33}_{1'01}\right) \frac{\partial^2 w}{\partial z^2}$$

$$+ 4 a c k^{31}_{101} \frac{\partial^2 u}{\partial x \partial z} + 4 b c k^{31}_{1'01} \frac{\partial^2 u}{\partial y \partial z} + 4 b c \left(k^{32}_{011} + k^{32}_{1'01}\right) \frac{\partial^2 v}{\partial y \partial z} \qquad 2.68$$

Newton's law for the force components in the directions x, y and z may, of course, be written as

$$\frac{F_x}{abc} = \rho \ddot{u}$$

$$\frac{F_y}{abc} = \rho \ddot{v}$$

and

$$\frac{F_z}{abc} = \rho \ddot{w} \qquad 2.69$$

where abc = volume of a unit cell.

The corresponding continuum equations 2.25 based on the generalized Hooke's law are relisted below to facilitate comparison:

$$\rho \ddot{u} = c_{11} \frac{\partial^2 u}{\partial x^2} + c_{66} \frac{\partial^2 u}{\partial y^2} + c_{55} \frac{\partial^2 u}{\partial z^2} + (c_{12} + c_{66}) \frac{\partial^2 v}{\partial x \partial y} + (c_{13} + c_{55}) \frac{\partial^2 w}{\partial x \partial z}$$

$$\rho \ddot{v} = c_{66} \frac{\partial^2 v}{\partial x^2} + c_{22} \frac{\partial^2 v}{\partial y^2} + c_{44} \frac{\partial^2 v}{\partial z^2} + (c_{12} + c_{66}) \frac{\partial^2 u}{\partial x \partial y} + (c_{23} + c_{44}) \frac{\partial^2 w}{\partial y \partial z}$$

$$\rho \ddot{w} = c_{55} \frac{\partial^2 w}{\partial x^2} + c_{44} \frac{\partial^2 w}{\partial y^2} + c_{33} \frac{\partial^2 w}{\partial z^2} + (c_{13} + c_{55}) \frac{\partial^2 u}{\partial x \partial z} + (c_{23} + c_{44}) \frac{\partial^2 v}{\partial y \partial z}$$

Comparing coefficients in the two sets of equations we obtain the following expressions for the elastic constants c_{ij} in terms of the interaction constants $k^{ij}_{\ell mn}$:

$$c_{11} = \frac{a}{bc}\left(k^{11}_{100} + \frac{1}{2}k^{11}_{1'00} + 2k^{11}_{101} + k^{11}_{1'01}\right)$$

$$c_{66} = \frac{b}{ac}\left(k^{11}_{010} + \frac{1}{2}k^{11}_{1'00} + 2k^{11}_{011} + k^{11}_{1'01}\right) \qquad 2.70$$

$$c_{55} = \frac{c}{ab}\left(k^{11}_{001} + 2k^{11}_{101} + 2k^{11}_{011} + 4k^{11}_{1'01}\right)$$

$$c_{12} + c_{66} = 0$$

$$c_{13} + c_{55} = \frac{4}{b}k^{13}_{101}$$

$$c_{66} = \frac{a}{bc}\left(k^{22}_{100} + \frac{1}{2}k^{22}_{1'00} + k^{22}_{1'01}\right)$$

$$c_{22} = \frac{b}{ac}\left(k^{22}_{010} + \frac{1}{2}k^{22}_{1'00} + 2k^{22}_{011} + k^{22}_{1'01}\right) \qquad 2.71$$

$$c_{44} = \frac{c}{ab}\left(k^{22}_{001} + 2k^{22}_{011} + 4k^{22}_{1'01}\right)$$

$$c_{12} + c_{66} = 0$$

$$c_{23} + c_{44} = \frac{4}{a}\left(k^{23}_{011} + k^{23}_{1'01}\right)$$

$$c_{55} = \frac{a}{bc}\left(k^{33}_{100} + \frac{1}{2}k^{33}_{1'00} + 2k^{33}_{101} + k^{33}_{1'01}\right)$$

$$c_{44} = \frac{b}{ac}\left(k^{33}_{010} + \frac{1}{2}k^{33}_{1'00} + 2k^{33}_{011} + k^{33}_{1'01}\right) \qquad 2.72$$

$$c_{33} = \frac{c}{ab}\left(k^{33}_{001} + 2k^{33}_{101} + 2k^{33}_{011} + 4k^{33}_{1'01}\right)$$

$$c_{13} + c_{55} = \frac{4}{b}k^{31}_{101}$$

$$c_{23} + c_{44} = \frac{4}{a}\left(k^{32}_{011} + k^{32}_{1'01}\right)$$

These in turn may be combined and rewritten to give:

$$c_{11} = \frac{a}{bc}\,(k^{11}_{100} + \frac{1}{2}\,k^{11}_{1'00} + 2\,k^{11}_{101} + k^{11}_{1'01})$$

$$c_{22} = \frac{b}{ac}\,(k^{22}_{010} + \frac{1}{2}\,k^{22}_{1'00} + 2\,k^{22}_{011} + k^{22}_{1'01})$$

$$c_{33} = \frac{c}{ab}\,(k^{33}_{001} + 2\,k^{33}_{101} + 2\,k^{33}_{011} + 4\,k^{33}_{1'01})$$

$$c_{44} = \frac{c}{ab}\,(k^{22}_{001} + 2\,k^{22}_{011} + 4\,k^{22}_{1'01})$$

$$\text{or } c_{44} = \frac{b}{ac}\,(k^{33}_{010} + \frac{1}{2}\,k^{33}_{1'00} + 2\,k^{33}_{011} + k^{33}_{1'01})$$

$$c_{55} = \frac{c}{ab}\,(k^{11}_{001} + 2\,k^{11}_{101} + 2\,k^{11}_{011} + 4\,k^{11}_{1'01})$$

$$\text{or } c_{55} = \frac{a}{bc}\,(k^{33}_{100} + \frac{1}{2}\,k^{33}_{1'00} + 2\,k^{33}_{101} + k^{33}_{1'01}) \qquad 2.73$$

$$c_{66} = \frac{b}{ac}\,(k^{11}_{010} + \frac{1}{2}\,k^{11}_{1'00} + 2\,k^{11}_{011} + k^{11}_{1'01})$$

$$\text{or } c_{66} = \frac{a}{bc}\,(k^{22}_{100} + \frac{1}{2}\,k^{22}_{1'00} + k^{22}_{1'01})$$

$$c_{12} = -\,c_{66}$$

$$c_{13} = \frac{4}{b}\,k^{13}_{101} - c_{55}$$

$$= \frac{4}{b}\,k^{31}_{101} - c_{55}$$

$$c_{23} = \frac{4}{a}\,(k^{23}_{011} + k^{23}_{1'01}) - c_{44}$$

$$= \frac{4}{a}\,(k^{32}_{011} + k^{32}_{1'01}) - c_{44}$$

The expressions 2.73 may be simplified by excluding the terms involving the second nearest neighbor interactions; this yields the following expressions for first nearest-neighbor interactions:

$$c_{11} = \frac{a}{bc}\left(k^{11}_{100} + \frac{1}{2}\,k^{11}_{1'00}\right)$$

$$c_{22} = \frac{b}{ac}\left(k^{22}_{010} + \frac{1}{2}\,k^{22}_{1'00}\right)$$

$$c_{33} = \frac{c}{ab}\,k^{33}_{001}$$

$$c_{44} = \frac{c}{ab}\,k^{22}_{001} \text{ or } = \frac{b}{ac}\left(k^{33}_{010} + \frac{1}{2}\,k^{33}_{1'00}\right) \qquad 2.74$$

$$c_{55} = \frac{c}{ab}\,k^{11}_{001} \text{ or } = \frac{a}{bc}\left(k^{33}_{100} + \frac{1}{2}\,k^{33}_{1'00}\right)$$

$$c_{66} = \frac{b}{ac}\left(k^{11}_{010} + \frac{1}{2}\,k^{11}_{1'00}\right) \text{ or } = \frac{a}{bc}\left(k^{22}_{100} + \frac{1}{2}\,k^{22}_{1'00}\right)$$

$$c_{12} = -\,c_{66}$$

$$c_{13} = -\,c_{55}$$

$$c_{23} = -\,c_{44}$$

Constants c_{44}, c_{55} and c_{66}, and correspondingly c_{12}, c_{13} and c_{23} are double-valued. An appropriate single numerical value will be selected for these later in Section 2.5.

Central Force Assumption

If only central forces are allowed, the following sixteen of the thirty interaction constants entering Equations 2.54-59 vanish:

$$k^{11}_{010},\ k^{13}_{101},\ k^{11}_{011},\ k^{13}_{1'01},\ k^{12}_{101},\ k^{22}_{100},\ k^{23}_{011},\ k^{21}_{1'01},\ k^{23}_{1'01},$$

$$k^{33}_{100},\ k^{33}_{010},\ k^{33}_{1'00},\ k^{31}_{101},\ k^{32}_{011},\ k^{32}_{1'01},\ k^{31}_{1'01}\ ; \qquad 2.75$$

while the following fourteen will still be involved:

$$k^{11}_{100},\ k^{11}_{001},\ k^{11}_{1'00},\ k^{11}_{101},\ k^{11}_{1'01},\ k^{22}_{010},\ k^{22}_{001},$$
$$k^{22}_{1'00},\ k^{22}_{011},\ k^{22}_{1'01},\ k^{33}_{001},\ k^{33}_{101},\ k^{33}_{011},\ k^{33}_{1'01} \qquad 2.76$$

It may be noted that, unlike nonpolymeric crystals, the constants k^{11}_{001} and k^{22}_{001} do not vanish because of the bending resistance of the C-C bonds. This means that the central force assumption is being applied in a limited manner.

The expressions for the elastic constants c_{ij} under this central force assumption, including interactions up to second nearest-neighbors, become:

$$c_{11} = \frac{a}{bc}\left(k^{11}_{100} + \frac{1}{2}\,k^{11}_{1'00} + 2\,k^{11}_{101} + k^{11}_{1'01}\right)$$
$$c_{22} = \frac{b}{ac}\left(k^{22}_{010} + \frac{1}{2}\,k^{22}_{1'00} + 2\,k^{22}_{011} + k^{22}_{1'01}\right)$$
$$c_{33} = \frac{c}{ab}\left(k^{33}_{001} + 2\,k^{33}_{101} + 2k^{33}_{011} + 4k^{33}_{1'01}\right)$$
$$c_{44} = \frac{c}{ab}\left(k^{22}_{001} + 2\,k^{22}_{011} + 4\,k^{22}_{1'01}\right)$$
$$\text{or } c_{44} = \frac{b}{ac}\left(2\,k^{33}_{011} + k^{33}_{1'01}\right)$$
$$c_{55} = \frac{c}{ab}\left(k^{11}_{001} + 2\,k^{11}_{101} + 4\,k^{11}_{1'01}\right. \qquad 2.77$$
$$\text{or } c_{55} = \frac{a}{bc}\left(2\,k^{33}_{101} + k^{33}_{1'01}\right)$$
$$c_{66} = \frac{b}{ac}\left(\frac{1}{2}\,k^{11}_{1'00} + k^{11}_{1'01}\right)$$
$$\text{or } c_{66} = \frac{a}{bc}\left(\frac{1}{2}\,k^{22}_{1'00} + k^{22}_{1'01}\right)$$
$$c_{12} = -\,c_{66}$$

Magnitudes of c_{23}, c_{13}, c_{12} are equal to those of c_{44}, c_{55}, c_{66} due to dropping the interaction constants for the central force assumption. This does not imply that the number of independent elastic constants is reduced to six.

$$c_{13} = -c_{55}$$

$$c_{23} = -c_{44}$$

But for first neighbors only these may be further simplified to give:

$$c_{11} = \frac{a}{bc}\left(k^{11}_{100} + \frac{1}{2}k^{11}_{1'00}\right)$$

$$c_{22} = \frac{b}{ac}\left(k^{22}_{010} + \frac{1}{2}k^{22}_{1'00}\right)$$

$$c_{33} = \frac{c}{ab}k^{33}_{001}$$

$$c_{44} = \frac{c}{ab}k^{22}_{001} \quad \text{or} \quad c_{44} = 0$$

$$c_{55} = \frac{c}{ab}k^{11}_{001} \quad \text{or} \quad c_{55} = 0$$

$$c_{66} = \frac{1}{2}\frac{b}{ac}k^{11}_{1'00} \text{ or } = \frac{1}{2}\frac{a}{bc}k^{22}_{1'00} \qquad 2.78$$

$$c_{12} = -c_{66}$$

$$c_{13} = -c_{55}$$

$$c_{23} = -c_{44}$$

These show that polyethylene single crystals possess shear resistance even when first nearest-neighbor interactions and central forces are assumed. It may also be remarked that identical expressions are obtained for first nearest-neighbors from strain energy considerations, as shown in Appendix III.

2.4. Interaction Constants and Molecular Force Constants

The elastic constants were related to the interaction constants in the last section, and in Section 2.2 it was explained that interaction forces result directly from relative motions of the lattice units in the intramolecular and intermolecular force fields. The objective of the present section is to obtain expressions for the interaction constants in terms both of the intramolecular force constants, such as those for C-C bond stretching, bending and repulsion, and the intermolecular force constants, such as those appearing in the Lennard-Jones potential.

It is assumed as before that the weak secondary bond forces between units lying on different chains are central. However, the same cannot be said of the forces between units lying along a single chain; these are due to the strong connecting C-C bonds which provide resistance to bending in lateral directions. For this reason the central force assumption is limited to intermolecular forces only.

The following interaction constants,

$$k^{11}_{100},\ k^{11}_{001},\ k^{11}_{1'00},\ k^{11}_{101},\ k^{11}_{1'01},\ k^{22}_{010},\ k^{22}_{001}$$

$$k^{22}_{1'00},\ k^{22}_{011},\ k^{22}_{1'01},\ k^{33}_{001},\ k^{33}_{101},\ k^{33}_{011},\ k^{33}_{1'01}$$

will be obtained in terms of the molecular force constants such as the C-C bond stretching, bending and repulsion force constants K, H and F, respectively, and the Lennard-Jones potential constants A and B. The rest of the interaction constants (listed in 2.75) vanish under the limited type of central forces that exist between the lattice units, as discussed in the preceding paragraph.

Constants Along the Chain

Of the fourteen interaction constants needed for interactions up to second nearest-neighbors under the central force assumption, three are for forces between units along the same chain, viz.,

$$k_{001}^{11},\ k_{001}^{22}\ \text{and}\ k_{001}^{33}\quad .$$

These will primarily involve the C-C bond constants. Further, if displacements remain small and the planar zigzag conformation of the polyethylene chain does not change, it may be assumed that no torsion takes place; and any deformation may be accomplished merely by stretching and bending the C-C bond. Thus, if as in Figure 2.10,

δr = change in the bond length r

$\delta \alpha$ = change in the bond angle $\alpha/2$

and

δd = change in the distance $\frac{d}{2}$ between two alternate C-atoms,

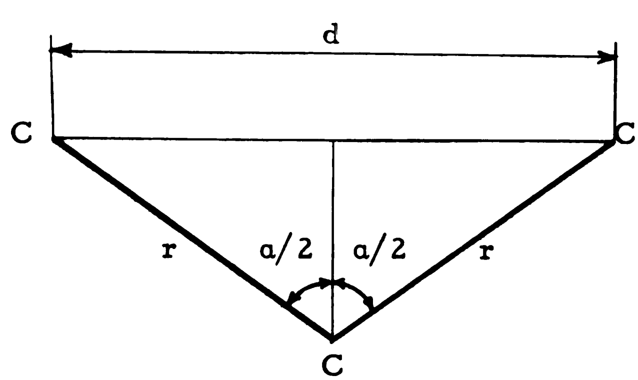


Figure 2.10. Geometry of two corresponding C-C bonds showing the bond length r, bond angle α and the distance between alternate C atoms.

the strain energy V becomes

$$V = 2[\frac{1}{2} K(\delta r)^2 + \frac{1}{2} H(r\delta\alpha)^2 - \frac{1}{2} F(\delta d)^2] \qquad 2.79$$

where K, H and F represent the stretching, bending and repulsive force constants.

To determine the interaction constants k_{001}^{11}, k_{001}^{22} and k_{001}^{33}, particular expressions for V must be derived by considering the respective deformations in the x, y and z-directions; these are illustrated below:

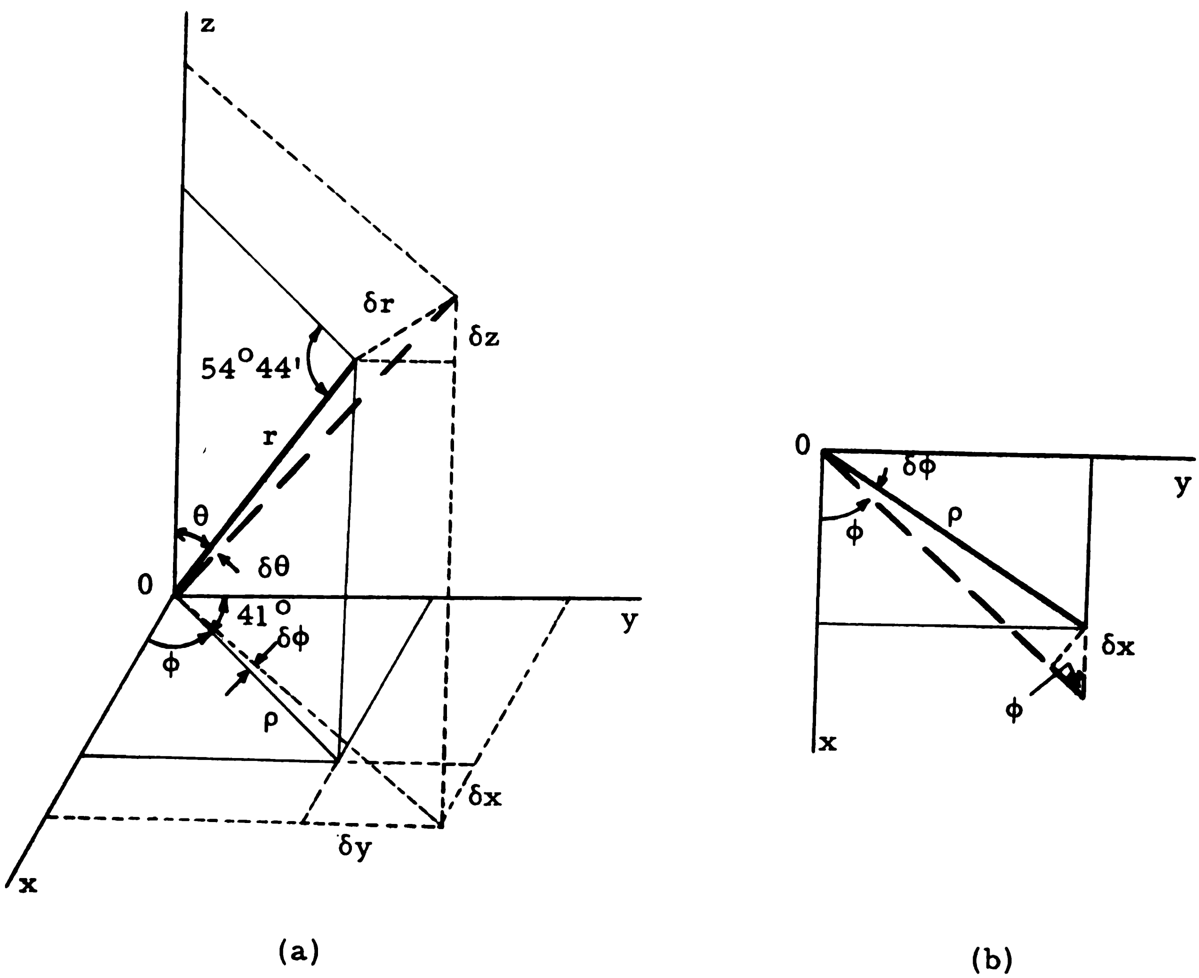
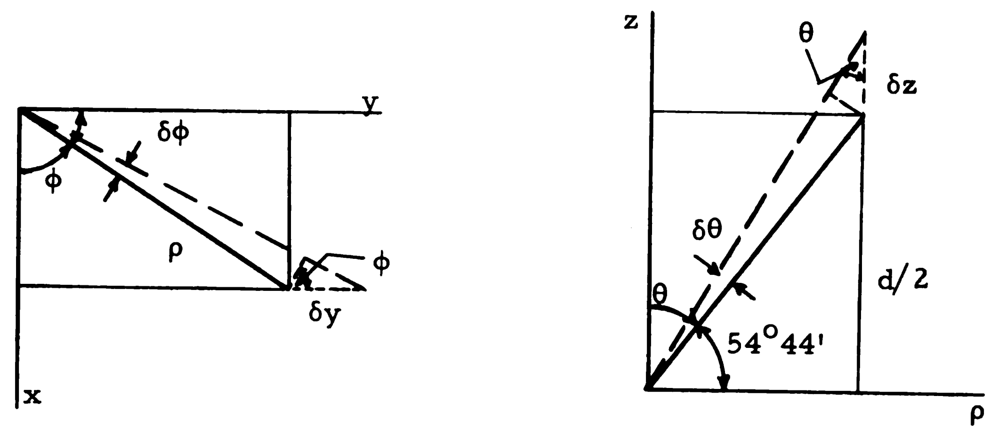


Figure 2.11. Deformation of C-C bonds (a) in a general direction (b) in x-direction only.



(c) (d)

Figure 2.11. Deformation of C-C bonds (c) in y-direction only (d) in z-direction only.

The Constant k_{001}^{11}

By definition, k_{001}^{11} is the force on the unit (0, 0, 0), per unit displacement u of the unit (0, 0, 1). Denoting this displacement by δx, as in Figure 2.11 (b), the quantities δr, δa and δd of Equation 2.78 may be obtained in the following way. Letting

$$\theta = \frac{\pi}{2} - \frac{a}{2} \quad ,$$

where $\frac{a}{2} = 54^{\circ}44'$,

$$\phi = \frac{\pi}{2} - 41^{\circ} = 49^{\circ} \quad .$$

The bond length r is given by

$$r^2 = x^2 + y^2 + z^2 \quad ;$$

and differentiating this expression we get

$$2r\,\delta r = 2x\,\delta x + 2y\,\delta y + 2z\,\delta z,$$

where for k^{11}_{001} , $\delta y = \delta z = 0$.

Therefore,

$$2r\,\delta r = 2x\,\delta x$$

or

$$\delta r = \frac{x}{r}\,\delta x \quad .$$

Now, since $\rho = r \cos(\alpha/2)$, as shown in Figure 2.11(a),

$$\frac{x}{r} = \frac{\rho \cos\phi}{r} = \frac{r}{r} \cos\frac{\alpha}{2} \cos\phi = \cos\frac{\alpha}{2} \cos\phi = \cos\frac{\alpha}{2} \sin 41^\circ ;$$

and we have

$$\begin{aligned} \delta r &= \cos\frac{\alpha}{2} \sin 41^\circ\,\delta x \\ &= \cos 54.7^\circ \sin 41^\circ\,\delta x \\ &= g\,\delta x \quad , \end{aligned}$$

where

$$g = \cos 54.7^\circ \sin 41^\circ \quad .$$

Also, from Figure 2.11 (b) we have

$$\begin{aligned} \delta\theta &= \frac{\cos 41^\circ}{r}\,\delta x \\ &= \frac{d}{r}\,\delta x \quad , \end{aligned}$$

where

$$d = \cos 41^\circ$$

and

$$\delta d = 0 \quad .$$

Consequently, substitution for δr, $\delta\theta$ or $\delta\alpha$, and δd in 2.79 yields

$$V = K(g\ \delta x)^2 + H(d\ \delta x)^2 \quad ; \qquad 2.80$$

and differentiating this with respect to δx, we get an expression for F_x:

$$F_x = -\frac{dV}{d\delta x} = -(2\ g^2 K + 2\ d^2 H)\ \delta x \qquad 2.81$$

Therefore, k_{001}^{11}, being the force per unit displacement, is given by

$$k_{001}^{11} = -\frac{F_x}{\delta x} = 2(g^2 K + d^2 H) \ . \qquad 2.82$$

The negative sign indicates attraction for positive displacement.

The Constant k_{001}^{22}

Following a procedure similar to the above for k_{001}^{11}, but considering only the displacement δy, analogous expressions for k_{001}^{22} may be obtained:

$$V = K(h\delta y)^2 + H(e\delta y)^2, \qquad 2.83$$

$$h = \cos 54.7^\circ \cos 41^\circ$$

$$e = \sin 41^\circ \quad .$$

$$F_y = -\frac{dV}{d\delta y} = -(2\,h^2\,K + 2\,e^2\,H)\,\delta y \qquad 2.84$$

$$k_{001}^{22} = 2\,(h^2K + e^2H) \qquad 2.85$$

The Constant k_{001}^{33}

Similarly, by considering only the displacement δz, the corresponding expressions for k_{001}^{33} can be derived:

$$V = K(i\delta z)^2 + H(f\delta z)^2 - F(\delta z)^2 \;, \qquad 2.86$$

$$i = \sin 54.7^\circ$$

$$f = \cos 54.7^\circ \;.$$

$$F_z = -(2\,i^2K + 2\,f^2H - \;F)\,\delta z \qquad 2.87$$

$$k_{001}^{33} = 2\,(i^2K + f^2\,H - 2\,F) \qquad 2.88$$

Other constants are essentially derived from the Lennard-Jones 6-12 potential curve $\phi(r)$ shown in Figure 2.3. This defines the force existing between the lattice units and its variation with separation distance as well. If the latter is less than the equilibrium distance r_o, the force will be repulsive and if it is greater than the equilibrium distance, it will be attractive. For the small displacements with which we are concerned, the force may be assumed to vary linearly, though the rate of variation will evidently be different for different separation distances. Such an assumption makes it possible to evaluate the interaction constants by determining the slope of the force curve at the various lattice distances. Thus, if F(r) is given by

$$F(r) = \frac{12A}{r^{13}} - \frac{6B}{r^7}, \qquad 2.28$$

then the derivative of $F(r)$ with respect to r is

$$\frac{dF}{dr} = -\frac{156A}{r^{14}} + \frac{42B}{r^8} \quad . \qquad 2.89$$

This determines the interaction constants for the first nearest-neighbors as

$$k^{11}_{100} = -\left(\frac{dF}{dr}\right)_{r=a} = \frac{156A}{a^{14}} - \frac{42B}{a^8} \qquad 2.90$$

and

$$k^{22}_{010} = -\left(\frac{dF}{dr}\right)_{r=b} = \frac{156A}{b^{14}} - \frac{42B}{b^8} \quad . \qquad 2.91$$

The interaction constants for the diagonal units and second nearest-neighbors are determined from the components of the diagonal force, or the force along the line joining the central unit with the surrounding units. Thus,

$$k^{11}_{1'00} = \frac{d}{dr}\left[\frac{a}{\sqrt{a^2+b^2}}\left(-\frac{12A}{r^{13}} + \frac{6B}{r^7}\right)\right]_{r=\frac{1}{2}\sqrt{a^2+b^2}},$$

giving:

$$k^{11}_{1'00} = \frac{a}{\sqrt{a^2+b^2}}\left[\frac{156A}{\left(\frac{a^2+b^2}{4}\right)^7} - \frac{42B}{\left(\frac{a^2+b^2}{4}\right)^4}\right] \qquad 2.92$$

$$k^{22}_{1'00} = \frac{b}{\sqrt{a^2+b^2}} \left[\frac{156A}{\left(\frac{a^2+b^2}{4}\right)^7} - \frac{42B}{\left(\frac{a^2+b^2}{4}\right)^4} \right] \quad 2.93$$

$$k^{11}_{101} = \frac{a}{\sqrt{a^2+c^2}} \left[\frac{156A}{\left(a^2+c^2\right)^7} - \frac{42B}{\left(a^2+c^2\right)^4} \right] \quad 2.94$$

$$k^{33}_{101} = \frac{c}{\sqrt{a^2+c^2}} \left[\frac{156A}{\left(a^2+c^2\right)^7} - \frac{42B}{\left(a^2+c^2\right)^4} \right] \quad 2.95$$

$$k^{22}_{011} = \frac{b}{\sqrt{b^2+c^2}} \left[\frac{156A}{\left(b^2+c^2\right)^7} - \frac{42B}{\left(b^2+c^2\right)^4} \right] \quad 2.96$$

$$k^{33}_{011} = \frac{c}{\sqrt{b^2+c^2}} \left[\frac{156A}{\left(b^2+c^2\right)^7} - \frac{42B}{\left(b^2+c^2\right)^4} \right] \quad 2.97$$

$$k^{11}_{1'01} = \frac{a}{\sqrt{a^2+b^2+4c^2}} \left[\frac{156A}{\left(\frac{a^2+b^2+4c^2}{4}\right)^7} - \frac{42B}{\left(\frac{a^2+b^2+4c^2}{4}\right)^4} \right] \quad 2.98$$

$$k^{22}_{1'01} = \frac{b}{\sqrt{a^2+b^2+4c^2}} \left[\frac{156A}{\left(\frac{a^2+b^2+4c^2}{4}\right)^7} - \frac{42B}{\left(\frac{a^2+b^2+4c^2}{4}\right)^4} \right] \quad 2.99$$

$$k^{33}_{1'01} = \frac{2c}{\sqrt{a^2+b^2+4c^2}} \left[\frac{156A}{\left(\frac{a^2+b^2+4c^2}{4}\right)^7} - \frac{42B}{\left(\frac{a^2+b^2+4c^2}{4}\right)^4} \right] \quad 2.100$$

Numerical values of the interaction constants will be obtained along with the other constants in the next section (2.5), by substituting the values of the intermolecular force constants A and B and the intramolecular force constants K, H and F.

2.5. Numerical Values of Constants

Expressions for the Lennard-Jones potential constants were derived in Section 2.2, while in Section 2.4 expressions for the interaction constants were obtained in terms of the C-C bond stretching, bending and repulsive force constants and geometric parameters such as bond length, bond angle, lattice distances and setting angle. The connection between the elastic constants and the interaction constants was established in Section 2.3. In the present section, numerical values for all of these constants are obtained: first the Lennard-Jones constants, secondly, the interaction constants, and lastly, the elastic constants.

Lennard-Jones Constants

In Section 2.2, the expressions for the Lennard-Jones potential constants A and B, 2.49 and 2.50,

$$B = \frac{2 M \delta^2}{N_A \rho A_{12-6}}$$

$$A = p B = \frac{2 p M \delta^2}{N_A \rho A_{12-6}} \quad ,$$

involve various quantities to which numerical values may now be assigned. The molecular weight M of the ($-C_2H_4-$) lattice units is:

$$M = 2x12+4 = 28 \qquad 2.101$$

Avogadro's number N_A is:

$$N_A = 6.0249 \times 10^{23} \qquad 2.102$$

The cohesive energy density δ^2 for polyethylene, determined experimentally by Small (16), is:

$$\delta^2 = 62 \ \text{cal/cm}^3 \qquad 2.103$$

$$= 2.595320 \times 10^9 \ \text{erg/cm}^3$$

$$= 2.595320 \times 10^{-15} \ \text{erg/A}^3$$

The density ρ of crystalline polyethylene varies from one manufacturer to another; however, the variation is small and one representative value, listed in the commercial bulletin of the Dow Chemical Company, Midland, Michigan (27), is:

$$\rho = 0.964 \ \text{gram/cm}^3 \qquad 2.104$$

The factor $A_{12-6} = p\,A_{12} - A_6$ has been evaluated in Appendix I; its value is:

$$A_{12-6} = 2.345833 \times 10^{-3} \ A^{-6} \qquad \text{I-35}$$

The factor $p = \frac{1}{2}(r_o)^6$ has also been evaluated in Appendix I:

$$p = 3.897619 \times 10^3 \ A^6 \qquad \text{I-34}$$

Substituting these values in the above expressions for B and A, yields:

$$B = 2.177300 \times 10^{-10} \text{ erg A}^6$$
$$= 2.177300 \times 10^{-58} \text{ erg cm}^6 \qquad 2.105$$
$$A = 8.486677 \times 10^{-7} \text{ erg A}^{12}$$
$$= 8.486677 \times 10^{-103} \text{ erg cm}^{12} \qquad 2.106$$

Interaction Constants

In Section 2.4 the interaction constants $k^{ij}_{\ell mn}$ have been divided into two categories:

(a) Interaction constants for units on the same chain.

(b) Interaction constants for units on different chains.

These are evaluated below.

(a) Expressions for constants in category (a) are derived in Section 2.4. These relations (2.82, 85 and 88) involve the C-C bond stretching, bending and repulsive force constants K, H and F which are given by Shimanouchi, et al (17):

$$K = 4.0 \times 10^{-3} \text{ dyne/A}$$
$$H = 0.11 \times 10^{-3} \text{ dyne/A} \qquad 2.107$$
$$F = 0.96 \times 10^{-3} \text{ dyne/A}$$

The geometric factors g, h, i, d, e and f, are defined in Section 2.4 in terms of the following (10,11):

$$\text{C-C bond length } r = 1.54 \text{ A}$$
$$\text{C-C bond angle } \alpha = 109^\circ 28' \qquad 2.108$$
$$\text{setting angle } \beta = 41^\circ$$

Substituting these values of r, α, β, we obtain:

$$g^2 = 0.143724$$
$$h^2 = 0.190197$$
$$i^2 = 0.666084 \qquad 2.109$$
$$d^2 = 0.569587$$
$$e^2 = 0.430414$$
$$f^2 = 0.333922$$

The interaction constants in category (a) thus turn out to be:

$$k_{001}^{11} = 1.275102 \times 10^{-3} \text{ dyne/A}$$
$$k_{001}^{22} = 1.616266 \times 10^{-3} \text{ dyne/A} \qquad 2.110$$
$$k_{001}^{33} = 3.482134 \times 10^{-3} \text{ dyne/A}$$

(b) The expressions for the constants in category (b) are given in Section 2.4 (2.90-2.100). Their numerical values may be obtained by substituting the values of the Lennard-Jones constants A and B from 2.105 and 2.106 and the lattice parameters a, b and c of 7.41A, 4.94A and 2.55A. The result is:

$$k_{100}^{11} = -9.180603 \times 10^{-8} \text{ dyne/A}$$
$$k_{010}^{22} = -1.371359 \times 10^{-8} \text{ dyne/A}$$
$$k_{1'00}^{11} = 4.219081 \times 10^{-6} \text{ dyne/A}$$
$$k_{1'00}^{22} = 2.809002 \times 10^{-6} \text{ dyne/A}$$
$$k_{101}^{11} = -6.075525 \times 10^{-8} \text{ dyne/A}$$
$$k_{101}^{33} = -2.090739 \times 10^{-8} \text{ dyne/A}$$
$$k_{011}^{22} = -4.538807 \times 10^{-7} \text{ dyne/A}$$

$$k^{33}_{011} = -2.342901 \times 10^{-7} \text{ dyne/A}$$

$$k^{11}_{1'01} = -2.843103 \times 10^{-7} \text{ dyne/A}$$

$$k^{22}_{1'01} = -1.895375 \times 10^{-7} \text{ dyne/A}$$

$$k^{33}_{1'01} = -1.956759 \times 10^{-7} \text{ dyne/A}$$

2.111

Elastic Constants

The expressions 2.77 for the elastic constants c_{ij} in terms of the interaction constants $k^{ij}_{\ell mn}$ and the lattice parameters a, b and c under the central force assumption as derived in Section 2.4, on substitution of the numerical values from above, yield the following values, including second nearest-neighbor interactions:

$$c_{11} = 0.948127 \times 10^{-6} \text{ dyne/A}^2$$

$$c_{22} = 0.288779 \times 10^{-6} \text{ dyne/A}^2$$

$$c_{33} = 2.422665 \times 10^{-4} \text{ dyne/A}^2$$

$$c_{44} = 1.123761 \times 10^{-4} \text{ dyne/A}^2 = -c_{23}$$

$$c_{55} = 0.886595 \times 10^{-4} \text{ dyne/A}^2 = -c_{13}$$

$$c_{66} = 6.515515 \times 10^{-7} \text{ dyne/A}^2 = -c_{12}$$

2.112

The corresponding expressions 2.78 for first neighbors only yield:

$$c_{11} = 1.186831 \times 10^{-6} \text{ dyne/A}^2$$

$$c_{22} = 0.363552 \times 10^{-6} \text{ dyne/A}^2$$

$$c_{33} = 2.423565 \times 10^{-4} \text{ dyne/A}^2$$

$$c_{44} = 1.124921 \times 10^{-4} \text{ dyne/A}^2 = -c_{23}$$

$$c_{55} = 0.887471 \times 10^{-4} \text{ dyne/A}^2 = -c_{13}$$

$$c_{66} = 7.006943 \times 10^{-7} \text{ dyne/A}^2 = -c_{12}$$

2.113

As observed earlier, the constants c_{44}, c_{55}, c_{66}, c_{12}, c_{23} and c_{13} are doubled-valued. However, the constants c_{44} and c_{55} should have much higher values than the constant c_{66}, because the former two involve movements of units belonging to the same chain. Thus, only the higher values of c_{44} and c_{55} are used; but in the case of c_{66}, for which the two values are of the same order of magnitude, the average value is taken.

Substituting the values of c_{ij} 2.17-19 yields:

$$E_1 = 0.377123 \times 10^{-6} \text{ dyne/A}^2$$

$$E_2 = 0.266161 \times 10^{-6} \text{ dyne/A}^2$$

$$E_3 = 2.388100 \times 10^{-4} \text{ dyne/A}^2$$

2.114

All the numerical values are given to six decimal places as a matter of calculational convenience only. These may be rounded off to three decimal places for future use without any loss of accuracy.

III. DISCUSSIONS OF RESULTS

3.1. Anisotropy of Polyethylene Single Crystals

Anisotropy of polyethylene single crystals is a compound effect depending on the inherent nature of the lattice structure and the directional molecular forces of different strengths that exist along the three lattice axes. The complex orthorhombic lattice of polyethylene (Figure 1.6), consisting of ($-C_2H_4-$) as the lattice units, has been converted into a simple orthorhombic lattice (Figure 2.1) by choosing, as a basis, the pair consisting of chains at the mid-point and the corner of the rectangle (a, b). An orthorhombic lattice structure has nine independent elastic constants c_{ij}, whereas cubic crystals have only three such constants. Thus, an orthorhombic lattice, by itself, is anisotropic in a manner which is more complex than the cubic lattice; and the situation is further complicated by the directional molecular forces that exist between the units themselves. However, this complexity has been reduced by approaching the problem from the continuum and the discontinuum points of view independently, then relating the results.

3.2. Continuum Theory of the Orthorhombic Lattice

Crystals having an orthorhombic lattice, irrespective of what the molecular forces are, would be expected to have different elastic moduli along the three lattice axes because of the inequality of the lattice parameters a, b and c. Thus, there are three Young's moduli and three shear moduli for such crystals; however, Poisson's ratios are six in number, because

$$\nu_{ij} = -\frac{\epsilon_i}{\epsilon_j} \neq -\frac{\epsilon_j}{\epsilon_i} = \nu_{ji} \quad .$$

A uniaxial tensile stress along the a-axis would cause a certain contraction along the b or c-axis, and this would be different from the one caused along the a-axis by a uniaxial stress in the b or c-directions.

Expressions 2.17-19, for E_1, E_2 and E_3 in terms of c_{ij}, have a common numerator but different denominators. Hence the expression 2.20, which relates all three Young's moduli, can be derived. The shear moduli G_{23}, G_{13} and G_{12} are equal to c_{44}, c_{55}, c_{66} respectively (2.11) due to the definition of the shear strains (2.5). Expressions 2.16, 2.16a for the six Poisson's ratios must be obtained in pairs by considering uniaxial stresses along the three axes each time, and by solving the resulting equations simultaneously.

The equations of motion, 2.25, and the expression for the strain energy, 2.22, are slightly more involved than the corresponding equations and expression for cubic crystals. The strain energy relation is only an approximation, because higher-order terms involving rotational or torsional and coupled deformations are neglected. This is the case for cubic crystals too.

It should be pointed out again that the constants c_{ij} differ, not only due to the inequality of the lattice parameters, but also due to the inequality of the molecular forces in various directions. This is discussed in more detail later when their relationship with the interaction constants is explained.

3.3. Molecular Forces

Both intramolecular and intermolecular forces are highly directional. The intramolecular or primary bond forces which exist along the molecular chain axis are due to the covalent C-C bonds. These are several times stronger than the intermolecular or the secondary bond forces existing between the chains. The latter are a net result of the London dispersion forces of attraction and the repulsive forces caused by the overlap of the electron clouds surrounding the nuclei. In fact, the intramolecular forces are so strong that to some extent they dominate the inherent anisotropy of the orthorhombic lattice.

Molecular chains take a planar zigzag configuration, when in a lattice; thereby preventing free rotation of the segments of the molecules about the C-C bonds. This gives the chains a definite resistance to deformation along the c-axis, which is also the chain axis, and to bending in the lateral directions a and b. The strength of the C-C bond for various types of deformations is fairly well known and the values of these constants are listed in Section 2.4.

The strength of the secondary bond forces is known only as a measure of the cohesive energy or the sublimation energy. These intermolecular forces have been assumed to be determined by a 6-12 Lennard-Jones potential, which involves two unknown constants. It should be noted that the value of the sublimation energy, as determined experimentally by Muller (28), is more than twice the value of the cohesive energy as determined experimentally by Small (16). However, the value of the latter quantity is more reliable; first, because it is the more recent of the two and, secondly, because it is verified theoretically by the latter author. Accordingly, Small's cohesive energy data is employed here.

Values of the Lennard-Jones potential constants A and B determined in this manner have the same order of mangitude as for solid argon. This is to be expected because the lattice energy is of the same order of magnitude (23).

The intermolecular forces of polyethylene arise from the interaction between the hydrogen atoms, which are attached to the carbon atoms of the molecular chain by covalent bonds formed by sharing a pair of electrons. Thus, the valence electron of hydrogen spends most of the time in the region between the carbon and hydrogen atoms and very little time outside this region. The result is that the dispersion type of van der Waals forces, which arise from the time-varying instantaneous electron configurations, are very weak--a condition existing in rare gases too, though for a different reason,

It has been emphasized that polyethylene single crystals have an entangled-rectangular lattice structure in which the planes of the chains have two orientations. This fact is not considered in the computation of the lattice energy of a unit in an infinite matrix. However, as illustrated in Appendix IV, the orientation of the chains becomes insignificant if one considers their interaction in more detail. The chains are situated in space in such a manner that for any two neighboring chains the hydrogen atoms are equidistant from each other. This determines the Lennard-Jones potential between chains; the net or effective potential for the two units has been obtained in Appendix IV.

A slightly different method than the usual low density gas approach (23) has been used to determine the two Lennard-Jones potential constants. By taking the equilibrium separation distance between the two nearest chains to determine the minimum in the potential curve, the ratio of the two constants is fixed. This leaves only one unknown constant, which is then determined by computing the crystal potential energy density and comparing it with the cohesive energy density. In the case of gases, the crystal potential energy or the lattice energy is first calculated from a general potential. Its value is then minimized to determine the value of the equilibrium separation in terms of the lattice energy and one unknown constant, which in turn is obtained from data for the second virial coefficient. However, this is not applicable to solids where the equilibrium separation and the separation for minimum crystal potential energy are identical.

The triple inverse power series involved in computing the crystal potential energy converge very rapidly. Their values have been obtained by splitting them into component single, double, and triple series. For evaluation of the single series, standard formulae are given in reference (29) by Knopp. To compute the sums of the double and triple series, they were terminated at a point beyond which the contribution of the terms is less than 0.000015 for the sixth power and less than 0.00000000024 for the twelfth power.

As the units of distance along the three axes $a/2$, $b/2$, and c have been used; these lead to the above-mentioned series. However, it is only for points for which the integers along the a and b-axes are even, that a real unit exists. This point has been taken into account in computing the sums of the series.

In order to compare the crystal potential energy with the cohesive energy, all the units belonging to the central chains are ignored. These units are attached to each other permanently and remain so even when the chains are removed a considerable distance from each other, as required in determining the cohesive energy density.

3.4. Interaction Constants

To establish a relationship between the continuum elastic constants and the molecular force constants, first and second nearest-neighbor interactions have been considered. The expressions for the force components on a central unit due to its motion relative to its neighbors, involve thirty constants for interactions up to second nearest-neighbors, while for cubic crystals there are only five such constants. If only first neighbor interactions are considered, the expressions contain eleven constants for an orthorhombic crystal, whereas only two constants are involved in the case of cubic crystals.

In view of the inequality of the three lattice parameters a, b and c, all the first neighbors are not equidistant from the central unit. Such is the case for the second neighbors too. The first nearest-neighbors are the units which lie nearest to the central unit along the axes x, y, z, x' and x'' in either positive or negative directions. The second nearest-neighbors are the units that form rectangles with the first neighbors and the central unit. In this manner the four units corresponding to (1, 1, 0) are eliminated from the family of second nearest-neighbors, but the eight units corresponding to (1', 0, 1) are included instead.

A limited type of central force assumption has been applied to reduce the number of constants to fourteen for second nearest-neighbor interactions and seven for first nearest-neighbor interactions. The forces between the lattice units are not quite central, due to the units being rather unsymmetrical in shape. The major attractive forces arise from the hydrogen atoms which are located off the lattice points. However, because the forces between units belonging to different chains (secondary bond forces) are much smaller than the forces between units belonging to the same chain (primary bond forces), the former may be considered to be nearly central. This is what has been termed a limited type of central force assumption.

The interaction constants have, therefore, been classified in two categories:

(a) those for units belong to the same chain

(b) those for units belonging to different chains

The interaction constants of category (a) are obtained from the C-C bond stretching or contraction, bending and repulsive force constants, while those belonging to category (b) are obtained from the Lennard-Jones 6-12 potential.

All three constants of the first category, k^{11}_{001}, k^{22}_{001} and k^{33}_{001}, are positive and approximately 10^3 times stronger than $k^{11}_{1'00}$ and $k^{22}_{1'00}$, the only two positive constants of the second category. Other constants of the second category are negative, and their magnitudes are 10-100 times lower than these two.

As mentioned above, the constants $k^{11}_{1'00}$ and $k^{22}_{1'00}$ are positive, while the constants k^{11}_{100}, k^{22}_{010}, k^{11}_{101}, k^{33}_{101}, k^{22}_{011}, k^{33}_{011}, $k^{11}_{1'01}$, $k^{22}_{1'01}$ and $k^{33}_{1'01}$ are negative. The positive constants are for units whose separation distance is smaller than that to the point where the F(r) force curve has a zero slope. This occurs at a distance of $r = 4.493$ A -- slightly larger than the distance $r_o = 4.450$A, at which the $\phi(r)$ potential curve has a zero slope. Because the interaction constants are negative for units having a separation distance greater than $r = 4.493$A, it will be seen later that the inclusion of second nearest-neighbor interactions lowers the values of the elastic constants instead of raising them.

The interaction constants k^{11}_{001}, k^{22}_{001} and k^{33}_{001} involve deformations of the C-C bonds and, thus, are obtained from the strain energy expressions in terms of the particular type of deformation required. Identical results would be obtained if a general expression for the strain energy involving all types of C-C bond deformation were obtained. The constants could then be obtained by taking the appropriate partial derivative, though the expressions would be slightly more involved than the one used here.

The interaction constants k^{11}_{100}, k^{22}_{010}, $k^{11}_{1'00}$, $k^{22}_{1'00}$, k^{11}_{101}, k^{33}_{101}, k^{22}_{011}, k^{33}_{011}, $k^{11}_{1'01}$, $k^{22}_{1'01}$ and $k^{33}_{1'01}$ have been determined from the slopes of the force curve at the appropriate separation distances. Of course, this amounts to approximating the force curve by straight line segments in the neighborhood of the location of the units. However, for the infinitesimal displacements we are concerned with, this assumption is well justified.

3.5. Elastic Constants

Expressions for the nine elastic constants c_{ij} in terms of the interaction constants $k_{\ell mn}^{ij}$ have been derived in Section 2.3. These are obtained by comparing the coefficients of the appropriate partial derivatives in the equations of motion, derived from continuum theory, and the force components equations, derived from discontinuum theory. However, some of the partial derivatives appear twice in the equations of motion. This leads to redundant expressions for the constants c_{44}, c_{55} and c_{66} and, correspondingly, for the constants c_{23}, c_{13} and c_{12} also. Selection of the appropriate expressions was not made until their numerical values were obtained and a comparison could be made.

The expressions for the elastic constants have been simplified by employing the central force assumption discussed above to eliminate some of the constants, and these have been further simplified for first nearest-neighbor interactions. It may be pointed out that, for first neighbor interactions and the central force assumption, identical expressions are obtained from strain energy considerations in Appendix IV.

In order to decide upon one expression for the constants c_{44}, c_{55} and c_{66}, all the expressions were first evaluated by substituting in the values of interaction constants. The constants c_{44}, c_{55} and c_{66} are identified as the shear moduli. The first two involve movements of the units belonging to the same chain whereas the constant c_{66} involves movements of units on different chains. Thus, the values of c_{44} and c_{55} should be much higher than that of c_{66}.

However, c_{66} has two numerical values, both of the same order of magnitude; and in the absence of any criterion for making a selection, it was decided to use an average of the two values as the true value for this constant. The two lower values of c_{44} and c_{55} compare well with this value of c_{66}; however, their higher values are about 10^3 times larger. This suggests that the higher values of the constants are the right ones.

As mentioned earlier, because the interaction constants are negative for all units whose separation distance is greater than 4.493A, the numerical values of the elastic constants for second neighbor interactions are smaller than those for first neighbor interactions. Thus, it appears that the crystal gets weaker as one includes higher neighbor interactions, but the fact is that, as one includes interactions of all the surrounding units in an infinite matrix, the actual value of the constant is obtained. However, the contribution of neighbors higher than second neighbors is negligible; because as one goes to larger distance, the force curve levels off and its slope rapidly approaches a zero value. Thus, the value of the constants obtained by including interactions up to second neighbors is very close to their true value.

If only first neighbor interactions are considered, cubic crystals have no resistance to shear; it is only when second nearest-neighbor interactions are included that shear resistance is introduced. In the case of orthorhombic crystals, however, shear resistance in all directions is present even when only first neighbor interactions are considered and forces are assumed to be central. This is due to the existence of a unit at the mid-point of the orthorhombic-lattice rectangle (a, b), and the restrictions imposed on the central force assumption in the direction of the chain axis.

The values of the constants c_{11}, c_{22} and c_{33} are calculated to be 0.948127×10^{-6}, 0.288729×10^{-6} and 2.422665×10^{-4} dyne/A^2. The numerical value of c_{33} is about 100-1000 times the value of c_{11} and c_{22} which is compatible with the ratio of the order of 50 for the C-C bond dissociation energy of 83 kcal/mole (13) and the cohesive energy of 1.736 kcal/mole (16). Also the value of $E_3 = 2.388100 \times 10^{-4}$ dyne/A^2 calculated from c_{ij} (2.10) is in good agreement with the observed value of $E = 2.6 \times 10^{-4}$ dyne/A^2 for oriented polyethylene, obtained recently by Sakarda et al. (17). Shimanouchi et al. (17) have also calculated a value of $E = 3.4 \times 10^{-4}$ dyne/A^2 for infinitely-long oriented polyethylene molecules, which is much higher than the experimentally-determined value.

The constants c_{44}, c_{55} and c_{66}, which are measures of the shear moduli, have numerical values of 1.123761×10^{-4}, 0.886595×10^{-4} and 6.515515×10^{-7} dyne/A^2. No experimental value is available with which these may be compared to draw any useful conclusion. However, the values of the constants c_{44} and c_{55} are about 100-200 times the value of the constant c_{66}. This is reasonable because the former two involve movements of the units belonging to the same chain, and are thus connected by stronger C-C bonds. Further, the values of these moduli are lower than the corresponding E_1, E_2 and E_3 values which is true in general for shear and Young's moduli of bulk polycrystalline materials.

IV. CONCLUSIONS

1. The constants A and B in the 6-12 Lennard-Jones potential,

$$\phi(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} ,$$

for forces existing between polyethylene chains in the crystal lattice are found to be

$$A = 8.48667 \times 10^{-7} \text{ erg/A}^{12}$$

and

$$B = 2.177300 \times 10^{-10} \text{ erg/A}^{6} .$$

They are of the same order of magnitude as those for argon, whose lattice energy is of the same order as the cohesive energy of polyethylene.

2. The ratio of the dissociation energy of the primary C-C bonds and the cohesive energy of the secondary bonds is found to be approximately fifty. Thus, the primary bonds, or intramolecular forces, are about fifty times as strong as the secondary bonds, or intermolecular forces, for polyethylene single crystals.

3. For second nearest-neighbor interactions, thirty interaction constants have been found for polyethylene single crystals, as compared to only five such constants for crystals having simple cubic symmetry. For first neighbor interactions only, these constants become eleven in number, as against two for cubic crystals. On application of a limited central force assumption to the forces between units belonging to different chains, the numbers of constants for second nearest-

neighbors have been reduced to fourteen for polyethylene single crystals and two for cubic crystals. In the latter case, however, no limitation is imposed on the central force assumption. The corresponding numbers for the first neighbors become seven and one.

4. Interaction constants for units belonging to the same chain turn out to be 10^3-10^5 times higher in value than those for units belonging to different chains, the former being of the order of 1-3 x 10^{-3} dyne/A, whereas the latter have a magnitude ranging from 3 x 10^{-6} to 9 x 10^{-8} dyne/A.

5. Interaction constants for units having a separation distance less than 4.493 A are positive, while for others having higher separation distances they are negative. The magnitudes of the positive constants are found to be approximately 300 times the magnitudes of the negative constants for separations up to the most distant second neighbor. For higher order neighbors this factor will be still higher; but the true values of the elastic constants are approached very rapidly. In fact, second nearest neighbor interactions give values of the constants which are quite close to their acutal values.

6. The value of the elastic constant c_{33} is found to be about 200-1000 times the values of the constants c_{11} and c_{22}. These constants are measures of the Young's moduli along their respective axes. The exact value of the former is

$$c_{33} = 2.422665 \times 10^{-4} \text{ dyne/A}^2 \quad ,$$

which yields a value of Young's modulus of $E_3 = 2.388100 \times 10^{-4}$ dyne/A^2 that agrees with the observed value of Young's modulus for oriented polyethylene of 2.6×10^{-4} dyne/A^2 and is lower than the value of 3.4×10^{-4} dyne/A^2 calculated by Shimanouchi (17).

Values of the constants c_{11} and c_{22} are found to be:

$$c_{11} = 0.948127 \times 10^{-6} \text{ dyne}/A^2$$

$$c_{22} = 0.288779 \times 10^{-6} \text{ dyne}/A^2$$

These yield values of the Young's moduli E_1 and E_2 as 0.377123×10^{-6} dyne/A^2 and 0.266161×10^{-6} dyne/A^2 and, thus, seem quite reasonable since the value of Young's modulus of bulk polyethylene is known to be about 10^{-5} dyne/A^2. This fall squarely between the minimum value of 0.266161×10^{-6} dyne/A^2 calculated for E_2 and the maximum value of 2.388100×10^{-4} dyne/A^2 calculated for E_3.

7. The constants c_{44}, c_{55} and c_{66} have been calculated to be:

$$c_{44} = 1.123761 \times 10^{-4} \text{ dyne}/A^2$$

$$c_{55} = 0.866595 \times 10^{-4} \text{ dyne}/A^2$$

$$c_{66} = 6.515515 \times 10^{-7} \text{ dyne}/A^2$$

Thus, polyethylene single crystals are found to have shear resistance even when only first nearest-neighbor interactions are considered and the central force assumption is applied. This is in direct contrast to cubic crystals, for which shear resistance is introduced by considering the second neighbor interactions. The shear moduli c_{44} and c_{55}, which involve movements of units belonging to the same

chain, are found to be about 100-200 times the shear modulus c_{66}, which involves movements of units belonging to different chains.

Due to the lattice units being of unsymmetrical shape, the forces between them are not quite central. It would be of considerable interest to determine the effect of these forces on the elastic constants of polyethylene single crystals. The interaction constants in such a case may be evaluated by taking their geometry and location into account.

Bulk polyethylene is made up of spherulites which consist of randomly-oriented lamellae of single crystals. A future study could be directed towards finding how the elastic properties of spherulites are related to those of single crystals. This information may in turn be related to the elastic properties of bulk polyethylene.

Investigations identical to the present work could be extended to include polymers having lattice structures such as tetragonal, hexagonal, monoclinic, triclinic, and rhombohedral. A comparison of the inherent anisotropies of these materials due to their lattice structures would then be possible.

In many crystalline polymers hydrogen bonding provides the intermolecular forces, which are much stronger than the London dispersion-type of van der Waals forces. An investigation of the influence of hydrogen bonding on the elastic properties and, hence, the anisotropy of such polymers would be of considerable interest.

Due to the lattice units being of unsymmetrical shape, the forces between them are not quite central. It would be of considerable interest to determine the effect of these forces on the elastic constants of polyethylene single crystals. The interaction constants in such a case may be evaluated by taking their geometry and location into account.

Bulk polyethylene is made up of spherulites which consist of randomly-oriented lamellae of single crystals. A future study could be directed towards finding how the elastic properties of spherulites are related to those of single crystals. This information may in turn be related to the elastic properties of bulk polyethylene.

Investigations identical to the present work could be extended to include polymers having lattice structures such as tetragonal, hexagonal, monoclinic, triclinic, and rhombohedral. A comparison of the inherent anisotropies of these materials due to their lattice structures would then be possible.

In many crystalline polymers hydrogen bonding provides the intermolecular forces, which are much stronger than the London dispersion-type of van der Waals forces. An investigation of the influence of hydrogen bonding on the elastic properties and, hence, the anisotropy of such polymers would be of considerable interest.

APPENDIX I

EVALUATION OF SERIES

In order to determine the Lennard-Jones 6-12 potential constants A and B (Section 2.2), it is required to evaluate the triple series

$$A_s = \sum_{\ell, m, n=-\infty}^{\infty} [(\ell e_1)^2 + (me_2)^2 + (ne_3)^2]^{-s/2} \qquad \text{I-1}$$

for $s = 6$ or 12, and where ℓ, m = both even or both odd, but $\neq 0$

and n = any integer.

As defined earlier,

$$e_1 = \frac{a}{2} = 3.705 \text{ A}$$

$$e_2 = \frac{b}{2} = 2.470 \text{ A}$$

$$e_3 = \frac{c}{2} = 2.550 \text{ A} \quad .$$

Dividing and multiplying by e_1^s, I-1 may be written as

$$A_s = e_1^{-s} \Sigma [\ell^2 + m^2 (\frac{e_2}{e_1})^2 + n^2 (\frac{e_3}{e_1})^2]^{-s/2} \quad . \qquad \text{I-2}$$

Substituting

$$(\frac{e_2}{e_1})^2 = (\frac{2.470}{3.705})^2 = 0.444$$

$$(\frac{e_3}{e_1})^2 = (\frac{2.555}{3.705})^2 = 0.474$$

in I-2, we get

$$A_s = e_1^{-s} \Sigma (\ell^2 + 0.444 m^2 + 0.474 n^2)^{-s/2} \qquad \text{I-3}$$

$$= e_1^{-s} A_s' \quad , \qquad \text{I-4}$$

where

$$A'_s = \Sigma\, (\ell^2 + 0.444\, m^2 + 0.474\, n^2)^{-s/2} \qquad \text{I-5}$$

with the same conditions on ℓ, m, n as in I-1.

This triple series of I-5 is separated into single, double and triple series to find its value. These component series are evaluated as follows:

<u>Single Series</u>

For $m, n = 0$, we have

$$\sum_{\ell=-\infty}^{\infty} \ell^{-s} = 2 \sum_{\ell=2}^{\infty} \ell^{-s} = 2\, a_s \quad , \qquad \text{I-6}$$

where

$$a_s = \sum_{\ell=2}^{\infty} \ell^{-s} \qquad \text{for } \ell = \text{even only}$$

or $\qquad\qquad$ I-7

$$a_{2\nu} = \sum_{n=1}^{\infty} \left(\frac{1}{2n}\right)^{2\nu} \qquad \text{for } n = \text{any integer and } s = 2\nu = \text{even} \;.$$

Similarly for $\ell, n = 0$, we have

$$\sum_{m=-\infty}^{\infty} (0.444\, m^2)^{-s/2} = 2\,(0.444)^{-s/2}\, a_s \,. \qquad \text{I-8}$$

An exact method of finding the value of this single series is given by Knopp (29), by which

$$\sum_{n=1}^{\infty} \frac{1}{n^{2\nu}} = (-1)^{\nu-1}\, \frac{(2\pi)^{2\nu}}{2.(2\nu)!}\, B_{2\nu} \quad , \qquad \text{I-9}$$

where n is any integer, and B's are Bernoullian numbers. The first few of these numbers are

$$B_o = 1,\ B_1 = \frac{1}{2},\ B_2 = \frac{1}{6},\ B_4 = -\frac{1}{30},\ B_6 = \frac{1}{42},\ B_{12} = -\frac{691}{2730}\ \ldots \qquad \text{I-10}$$

and

$$B_3 = B_5 = \ldots = B_{2\nu+1} = 0 \quad \text{for} \quad 2\nu + 1 \geq 3 .$$

Expression I-9 for odd terms only is

$$\sum_{n=1}^{\infty} \frac{1}{(2n-1)^{2\nu}} = (-1)^{\nu-1} \frac{(2\pi)^{2\nu} - \pi^{2\nu}}{2.(2\nu)!} \qquad \text{I-11}$$

This is obtained from I-9 by substracting the series for even terms

$$a_s = \sum_{n=1}^{\infty} \left(\frac{1}{2n}\right)^{2\nu} = (-1)^{\nu-1} \frac{\pi^{2\nu}}{2.(2\nu)!} B_{2\nu} \qquad \text{I-12}$$

Setting $s = 2\nu = 6$ in I-12 yields:

$$a_6 = \sum_{n=1}^{\infty} \frac{1}{(2n)^6} = (-1)^2 \frac{\pi^6}{2.(6)!} B_6 \qquad \text{I-13}$$

Substituting $B_6 = \frac{1}{42}$ from I-10 in I-13, we get

$$a_6 = 0.015895916 . \qquad \text{I-14}$$

Similarly for $s = 12$, we have:

$$a_{12} = \sum_{n=1}^{\infty} \frac{1}{(2n)^{12}} = (-1)^5 \frac{\pi^{12}}{2.(12)!} B_{12} \qquad \text{I-15}$$

Substituting $B_{12} = -\frac{691}{2730}$ from I-10 in I-15, we get

$$a_{12} = 0.000244198 . \qquad \text{I-16}$$

Double Series

For $n = 0$, we have

$$\sum_{\ell, m=-\infty}^{\infty} (\ell^2 + 0.444\, m^2)^{-s/2} =$$

$$4 \sum_{\ell, m=2}^{\infty} (\ell^2 + 0.444\, m^2)^{-s/2} = 4\, b_s\,, \qquad \text{I-17}$$

where

$$b_s = \sum_{\ell, m=2}^{\infty} (\ell^2 + 0.444\, m^2)^{-s/2} \text{ for } \ell, m = \text{even only.}$$

I-18

Similarly for $m = 0$, we have

$$\sum_{\ell, n=-\infty}^{\infty} (\ell^2 + 0.474\, n^2)^{-s/2} = 4\, b'_s\,, \qquad \text{I-19}$$

where

$$b'_s = \sum_{\ell=2, n=1}^{\infty} (\ell^2 + 0.474\, n^2)^{-s/2} \quad \text{for } \ell = \text{even only and } n = \text{any integer;}$$

I-20

and for $\ell = 0$, we have

$$\sum_{m, n=-\infty}^{\infty} (0.444\, m^2 + 0.474\, n^2)^{-s/2} = 4\, b''_s\,, \qquad \text{I-21}$$

where

$$b''_s = \sum_{m=2, n=1}^{\infty} (0.44\, m^2 + 0.474\, n^2)^{-s/2}$$

for m = even and
n = any integer.

I-22

The double series b_s, b'_s and b''_s are evaluated by direct summation, and to do this with reasonable accuracy all the terms whose contribution is

$$< \left(\frac{1}{40}\right)^3 \approx 0.000015 \qquad \text{for } s = 6,$$

and is

$$< \left(\frac{1}{40}\right)^6 \approx 0.00000000024 \quad \text{for } s = 12,$$

are neglected. Such a termination of these sums is justifiable because of the fast convergence of the series. Though the number of terms increases rapidly with the increasing values of ℓ, m and n, the order of error involved would still be small because, first, the size of the polyethylene crystals is small (being finite) and, secondly, the contribution of only the first few terms is significant as compared to higher order terms.

Thus:

$$\begin{aligned} b_6 &= 0.34911017055 \\ b_{12} &= 0.101079817615962 \\ b'_6 &= 0.01782841530 \\ b'_{12} &= 0.000115699514101 5 \\ b''_6 &= 0.1201500514 \\ b''_{12} &= 0.00814363299990 3 \end{aligned} \qquad \text{I-23}$$

<u>Triple Series</u>

We have

$$\sum_{\ell, m, n=-\infty}^{\infty} (\ell^2 + 0.444\, m^2 + 0.474\, n^2)^{-s/2} = 8\, c_s \;, \qquad \text{I-24}$$

where

$$c_s = \sum_{\ell, m=2, n=1}^{\infty} (\ell^2 + 0.444\, m^2 + 0.474\, n^2)^{-s/2}$$

for ℓ, m = even and
n = any integer.

I-25

Evaluating the sums c_s with the same order of accuracy as for double series, we have:

$$c_6 = 0.20449870704$$
$$c_{12} = 0.0209123979253897 \qquad \text{I-26}$$

Rewriting the A'_s of I-5 as

$$A'_s = \sum_{\ell, m, n=-\infty}^{\infty} (\ell^2 + 0.444\, m^2 + 0.474\, n^2)^{-s/2}$$
$$= 2 \sum_{\ell=2}^{\infty} \ell^{-s} + 2 \sum_{m=2}^{\infty} (0.444\, m^2)^{-s/2}$$
$$+ 4 \sum_{\ell, m=2}^{\infty} (\ell^2 + 0.444\, m^2)^{-s/2} + 4 \sum_{\ell=2, n=1}^{\infty} (\ell^2 + 0.474\, n^2)^{-s/2}$$
$$+ 4 \sum_{m=2, n=1}^{\infty} (0.444\, m^2 + 0.474\, n^2)^{-s/2}$$
$$+ 8 \sum_{\ell, m=2, n=1}^{\infty} (\ell^2 + 0.444\, m^2 + 0.474\, n^2)^{-s/2}, \qquad \text{I-27}$$

we have

$$A'_s = 2\,(1 + 0.444^{-s/2})\, a_s + 4\,(b_s + b'_s + b''_s) + 8\, c_s\,.$$

I-28

Substituting

$$0.444^{-3} = 0.087528384 \quad \text{for} \quad s = 6$$

and

$$0.444^{-6} = 0.0076612 \quad \text{for} \quad s = 12$$

in I-28, we have

$$A'_6 = 2.175056768\, a_6 + 4\,(b_6 + b'_6 + b''_6) + 8\, c_6$$

and

$$A'_{12} = 2.0153224\, a_{12} + 4\,(b_{12} + b'_{12} + b''_{12}) + 8\, c_{12}\,, \tag{I-29}$$

while substituting the numerical values of a_s, b_s, b'_s, b''_s, c_s in the above, yields:

$$\begin{aligned} A'_6 &= 3.97935343732 \\ A'_{12} &= 0.66731910792 29836 \end{aligned} \tag{I-30}$$

To obtain numerical values of the sums A_s, these numerical values of A'_s must be substituted. Thus, for $s = 12$ and 6

$$A_{12} = e_1^{-12} \quad A'_{12}$$

and

$$A_6 = e_1^{-6} \quad A'_6 \;, \tag{I-31}$$

where

$$e_1 = 3.705\ \text{A}$$

such that

$$e_1^{-12} = 2,587.95131^{-2} \quad \text{A}^{-12}$$

and

$$e_1^{-6} = 2,587.95131^{-1} \quad \text{A}^{-6}\,. \tag{I-32}$$

Substituting I-32 in I-31 gives

$$A_{12} = 9.96372 \times 10^{-8} \quad A^{-12}$$

and I-33

$$A_6 = 1.537646 \times 10^{-3} \quad A^{-6} \quad .$$

Now, from 2.43 ,

$$A_{12-6} = p\, A_{12} - A_6 \ ,$$

where

$$p = \frac{1}{2}\ (r_o)^6 = \frac{1}{2}\ (4.45)^6 = \frac{1}{2}\ (7,795.23947455)$$

$$= 3,897.6197 \quad A^6 \ ; \qquad \text{I-34}$$

therefore,

$$A_{12-6} = -1.149298 \times 10^{-3} \quad A^{-6} \quad . \qquad \text{I-35}$$

APPENDIX II

TRANSFORMATION OF PARTIAL DERIVATIVES

Let c_{ij} be the direction cosines of the axes x', y', z', with respect to the axes x, y, z, as illustrated in the figure given below showing only the x' axis.

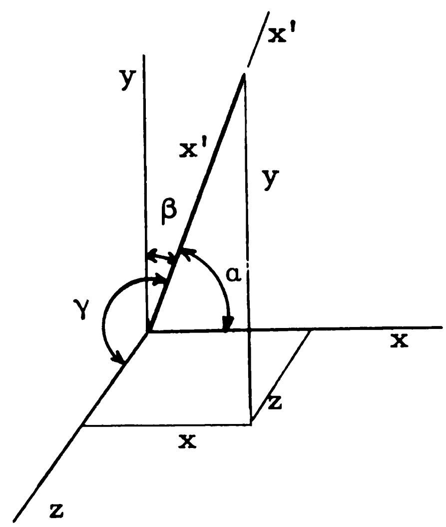


Figure II-1. Rotation of axes.

Thus,

$$c_{11} = \cos \alpha, \qquad c_{12} = \cos \beta, \qquad c_{13} = \cos \gamma \qquad \text{II-1}$$

such that

$$\begin{aligned} x &= c_{11}\, x' + c_{21}\, y' + c_{31}\, z' \\ y &= c_{12}\, x' + c_{22}\, y' + c_{32}\, z' \\ z &= c_{13}\, x' + c_{23}\, y' + c_{33}\, z' \end{aligned} \qquad \text{II-2}$$

Differentiating II-2 with respect to x, y, z, respectively, yields

$$\frac{\partial x}{\partial x'} = c_{11}, \qquad \frac{\partial y}{\partial x'} = c_{21}, \qquad \frac{\partial z}{\partial x'} = c_{31} \; . \qquad \text{II-3}$$

If a displacement function q is given as

$$q = q\,(x, y, z) \qquad \text{II-4}$$

then

$$\frac{\partial q}{\partial x'} = \frac{\partial q}{\partial x}\frac{\partial x}{\partial x'} + \frac{\partial q}{\partial y}\frac{\partial y}{\partial x'} + \frac{\partial q}{\partial x}\frac{\partial z}{\partial x'} \quad . \qquad \text{II-5}$$

Substituting from II-3 into II-5 results in

$$\frac{\partial q}{\partial x'} = c_{11}\frac{\partial q}{\partial x} + c_{21}\frac{\partial q}{\partial y} + c_{31}\frac{\partial q}{\partial z} \quad ; \qquad \text{II-6}$$

and differentiating II-6 again, we get

$$\begin{aligned}\frac{\partial^2 q}{\partial x'^2} = \frac{\partial}{\partial x'}\left(\frac{\partial q}{\partial x'}\right) &= c_{11}\left(c_{11}\frac{\partial^2 q}{\partial x^2} + c_{21}\frac{\partial^2 q}{\partial x \partial y} + c_{31}\frac{\partial^2 q}{\partial x \partial z}\right) \\ &+ c_{21}\left(c_{11}\frac{\partial^2 q}{\partial x \partial y} + c_{21}\frac{\partial^2 q}{\partial y^2} + c_{31}\frac{\partial^2 q}{\partial y \partial z}\right) \\ &+ c_{31}\left(c_{11}\frac{\partial^2 q}{\partial x \partial z} + c_{21}\frac{\partial^2 q}{\partial y \partial z} + c_{31}\frac{\partial^2 q}{\partial z^2}\right) \\ = c_{11}^2\frac{\partial^2 q}{\partial x^2} + c_{21}^2\frac{\partial^2 q}{\partial y^2} &+ c_{31}^2\frac{\partial^2 q}{\partial z^2} + 2c_{11}c_{21}\frac{\partial^2 q}{\partial x \partial y} \\ &+ 2\,c_{11}c_{31}\frac{\partial^2 q}{\partial x \partial z} + 2\,c_{21}c_{31}\frac{\partial^2 q}{\partial y \partial z} .\end{aligned}$$

II-7

It is required to transform second partial derivatives of the displacements with respect to the axes x_{12}, x_{21}; x_{13}, x_{31}; x_{23}, x_{32}; $x_{1'3}$, $x_{31'}$; $x_{1''3}$, $x_{31''}$ into partial derivatives with respect to x, y, z. In order to do so, the direction cosines of these axes are needed. They are listed below along with the corresponding axes.

$$x_{12} \; : \; \left(\frac{a}{\sqrt{a^2+b^2}} , \frac{b}{\sqrt{a^2+b^2}} , 0 \right)$$

$$x_{21} \; : \; \left(-\frac{a}{\sqrt{a^2+b^2}} , \frac{b}{\sqrt{a^2+b^2}} , 0 \right)$$

$$x_{13} \; : \; \left(\frac{a}{\sqrt{a^2+c}} , 0 , \frac{c}{\sqrt{a^2+c^2}} \right)$$

$$x_{31} \; : \; \left(-\frac{a}{\sqrt{a^2+c^2}} , 0 , \frac{c}{\sqrt{a^2+c^2}} \right)$$

$$x_{23} \; : \; \left(0 , \frac{b}{\sqrt{b^2+c^2}} , \frac{c}{\sqrt{b^2+c^2}} \right)$$

$$x_{32} \; : \; \left(0 , -\frac{b}{\sqrt{b^2+c^2}} , \frac{c}{\sqrt{b^2+c^2}} \right)$$

$$x_{1'3} \; : \; \left(\frac{a}{\sqrt{a^2+b^2+4c^2}} , \frac{b}{\sqrt{a^2+b^2+4c^2}} , \frac{c}{\sqrt{a^2+b^2+4c^2}} \right)$$

$$x_{31'} \; : \; \left(-\frac{a}{\sqrt{a^2+b^2+4c^2}} , -\frac{b}{\sqrt{a^2+b^2+4c^2}} , \frac{c}{\sqrt{a^2+b^2+4c^2}} \right)$$

$$x_{1''3} \; : \; \left(-\frac{a}{\sqrt{a^2+b^2+4c^2}} , \frac{b}{\sqrt{a^2+b^2+4c^2}} , \frac{2c}{\sqrt{a^2+b^2+4c^2}} \right)$$

$$x_{31''} \; : \; \left(\frac{a}{\sqrt{a^2+b^2+4c^2}} , -\frac{b}{\sqrt{a^2+b^2+4c^2}} , \frac{2c}{\sqrt{a^2+b^2+4c^2}} \right)$$

II-8

Thus, for differentiation with respect to the x_{12} axis, we have

$$\frac{\partial q}{\partial x_{12}} = \frac{\partial q}{\partial x'} = \frac{a}{\sqrt{a^2+b^2}} \frac{\partial q}{\partial x} + \frac{b}{\sqrt{a^2+b^2}} \frac{\partial q}{\partial y}$$

and differentiating again

$$\frac{\partial q}{\partial x_{12}^2} = \frac{\partial}{\partial x'} \left(\frac{\partial q}{\partial x'}\right) = \frac{a}{\sqrt{a^2+b^2}} \left(\frac{a}{\sqrt{a^2+b^2}} \frac{\partial^2 q}{\partial x^2} + \frac{b}{\sqrt{a^2+b^2}} \frac{\partial^2 q}{\partial x \partial y} \right)$$

$$+ \frac{b}{\sqrt{a^2+b^2}} \left(\frac{a}{\sqrt{a^2+b^2}} \frac{\partial^2 q}{\partial x \partial y} + \frac{b}{\sqrt{a^2+b^2}} \frac{\partial^2 q}{\partial y^2} \right) ,$$

or

$$\frac{\partial^2 q}{\partial x_{12}^2} = \frac{1}{a^2+b^2} \left(a^2 \frac{\partial^2 q}{\partial x^2} + 2ab \frac{\partial^2 q}{\partial x \partial y} + b^2 \frac{\partial^2 q}{\partial y^2} \right) . \qquad \text{II-9}$$

Similarly for the axis x_{21}

$$\frac{\partial^2 q}{\partial x_{21}^2} = \frac{1}{a^2+b^2} \left(a^2 \frac{\partial^2 q}{\partial x^2} - 2ab \frac{\partial^2 q}{\partial x \partial y} + b^2 \frac{\partial^2 q}{\partial y^2} \right) . \qquad \text{II-10}$$

Adding II-9 and II-10 yields

$$\frac{\partial^2 q}{\partial x_{12}^2} + \frac{\partial^2 q}{\partial x_{21}^2} = \frac{1}{a^2+b^2} \left(2\, a^2 \frac{\partial^2 q}{\partial x^2} + 2\, b^2 \frac{\partial^2 q}{\partial y^2} \right) , \qquad \text{II-11}$$

and subtracting II-10 from II-9 gives

$$\frac{\partial q}{\partial x_{12}^2} - \frac{\partial^2 q}{\partial x_{21}^2} = \frac{4\, ab}{a^2+b^2} \frac{\partial^2 q}{\partial x \partial y} . \qquad \text{II-12}$$

Repeating the above operation for the other sets, we have

$$\frac{\partial^2 q}{\partial x_{13}^2} + \frac{\partial^2 q}{\partial x_{31}^2} = \frac{1}{a^2+b^2} \left(2\, a^2 \frac{\partial^2 q}{\partial x^2} + 2\, c^2 \frac{\partial^2 q}{\partial z^2} \right) , \qquad \text{II-13}$$

$$\frac{\partial^2 q}{\partial x_{13}^2} - \frac{\partial^2 q}{\partial x_{31}^2} = \frac{4\,ac}{a^2+c^2} \quad \frac{\partial^2 q}{\partial x \partial z} \quad ; \qquad \text{II-14}$$

$$\frac{\partial^2 q}{\partial x_{23}^2} + \frac{\partial^2 q}{\partial x_{32}^2} = \frac{1}{b^2+c^2} \left(2\,b^2 \,\frac{\partial^2 q}{\partial y^2} + 2\,c^2\, \frac{\partial^2 q}{\partial z^2}\right) , \qquad \text{II-15}$$

$$\frac{\partial^2 q}{\partial x_{23}^2} - \frac{\partial^2 q}{\partial x_{32}^2} = \frac{4bc}{b^2+c^2} \quad \frac{\partial^2 q}{\partial y \partial z} \quad ; \qquad \text{II-16}$$

$$\frac{\partial^2 q}{\partial x_{1'3}^2} + \frac{\partial^2 q}{\partial x_{31'}^2} = \frac{1}{a^2+b^2+4c^2} \left(2\,a^2 \frac{\partial^2 q}{\partial x^2} + 8\,ab \frac{\partial^2 q}{\partial x \partial y} + 2\,b^2 \frac{\partial^2 q}{\partial y^2} + 8\,c^2 \,\frac{\partial^2 q}{\partial z^2}\right) , \qquad \text{II-17}$$

$$\frac{\partial^2 q}{\partial x_{1'3}^2} - \frac{\partial^2 q}{\partial x_{31'}^2} = \frac{1}{a^2+b^2+4c^2} \left(8\,ac \frac{\partial^2 q}{\partial x \partial z} + 8\,bc \frac{\partial^2 q}{\partial y \partial z}\right) ; \qquad \text{II-18}$$

$$\frac{\partial^2 q}{\partial x_{1''3}^2} + \frac{\partial^2 q}{\partial x_{31''}^2} = \frac{1}{a^2+b^2+4c^2} \left(2\,a^2 \frac{\partial^2 q}{\partial x^2} - 8\,ab \frac{\partial^2 q}{\partial x \partial y} + 2\,b^2 \frac{\partial^2 q}{\partial y^2} + 8\,c^2 \,\frac{\partial^2 q}{\partial z^2}\right) , \qquad \text{II-19}$$

$$\frac{\partial^2 q}{\partial x_{1''3}^2} - \frac{\partial^2 q}{\partial x_{31''}^2} = \frac{1}{a^2+b^2+4c^2} \left(-\,8\,ac \frac{\partial^2 q}{\partial x \partial z} + 8\,bc \frac{\partial^2 q}{\partial y \partial z}\right) ; \qquad \text{II-20}$$

$$\left(\frac{\partial^2 q}{\partial x_{1'3}^2} + \frac{\partial^2 q}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 q}{\partial x_{1''3}^2} + \frac{\partial^2 q}{\partial x_{31''}^2}\right) = \frac{1}{a^2+b^2+4c^2} \left(4\,a^2 \frac{\partial^2 q}{\partial y^2} + 4\,b^2 \frac{\partial^2 q}{\partial y^2} + 16\,c^2 \frac{\partial^2 q}{\partial z^2}\right) ,$$

II-21

$$\left(\frac{\partial^2 q}{\partial x_{1'3}^2} - \frac{\partial^2 q}{\partial x_{31'}^2}\right) + \left(\frac{\partial^2 q}{\partial x_{1''3}^2} - \frac{\partial^2 q}{\partial x_{31''}^2}\right) = \frac{1}{a^2+b^2+4c^2} \left(16\,bc \frac{\partial^2 q}{\partial y \partial z}\right) .$$

II-22

Equations II-9 through II-22 are the transformation relations utilized in deriving the expressions 2.63-65 from 2.60-62.

APPENDIX III

STRAIN ENERGY CONNECTION BETWEEN THE ELASTIC AND INTERACTION CONSTANTS

In Section 2.3, the elastic constants were obtained in terms of the interaction constants from a comparison of the equations of motion derived from continuum and discontinuum theories. Second nearest-neighbor interactions were considered; and the expressions thus obtained were simplified for first nearest-neighbors only and a limited type of central force assumption. Expressions identical to these (2.78) may also be obtained from strain energy considerations. In this appendix an expression for the strain energy is derived by considering motions of the first nearest-neighbor lattice units relative to the central unit. This is then compared with the corresponding continuum Expressions 2.22 of the Section 2.1.

First nearest-neighbors surrounding a central unit (0, 0, 0) are shown in Figure 2.5 in Section 2.3. Using the same notations as were used for the second nearest-neighbors, the strain energy per lattice unit u_I in terms of displacements u, v, w and the interaction constants, under the central force assumption becomes:

$$
\begin{aligned}
u_I = {} & \frac{1}{2}\, k^{11}_{100}(u_{100} - u_{000})^2 + \frac{1}{2} k^{22}_{010}\,(v_{010} - v_{000})^2 \\
& + \frac{1}{2} k^{11}_{001}\,(u_{001} - u_{000})^2 + \frac{1}{2} k^{22}_{001}(v_{001} - v_{000})^2 + \frac{1}{2} k^{33}_{001}(w_{001} - w_{000})^2 \\
& + \frac{1}{2} k^{11}_{1'00}[(u_{1'00} - u_{000})^2 + (u_{1''00} - u_{000})^2] \\
& + \frac{1}{2} k^{22}_{1'00}\,[(v_{1'00} - v_{000})^2 + (v_{1''00} - v_{000})^2]
\end{aligned}
\qquad \text{III-1}
$$

By dividing each term of the above expression by the appropriate lattice distance and using the well known finite difference relations we obtain:

$$u_I = \frac{1}{2} a^2 k^{11}_{100} \left(\frac{\partial u}{\partial x}\right)^2 + \frac{1}{2} b^2 k^{22}_{010} \left(\frac{\partial v}{\partial y}\right)^2 + \frac{1}{2} c^2 \Big[k^{11}_{001} \left(\frac{\partial u}{\partial z}\right)^2 + k^{22}_{001} \left(\frac{\partial v}{\partial z}\right)^2 + k^{33}_{001} \left(\frac{\partial w}{\partial z}\right)^2 \Big]$$
$$+ \frac{a^2+b^2}{8} \Big\{ k^{11}_{1'00}\Big[\left(\frac{\partial u}{\partial x_{12}}\right)^2 + \left(\frac{\partial u}{\partial x_{21}}\right)^2\Big] + k^{22}_{1'00}\Big[\left(\frac{\partial v}{\partial x_{12}}\right)^2 + \left(\frac{\partial v}{\partial x_{21}}\right)^2\Big] \Big\} \qquad \text{III-2}$$

Once again,by transforming differentiations with respect to x_{12} and x_{21} into those with respect to x, y, z, III-2 may be written as:

$$u_I = \frac{1}{2} \Big\{ a^2 k^{11}_{100} \left(\frac{\partial u}{\partial x}\right)^2 + b^2 k^{22}_{010} \left(\frac{\partial v}{\partial y}\right)^2 + c^2 \Big[k^{11}_{001} \left(\frac{\partial u}{\partial z}\right)^2 + k^{22}_{001} \left(\frac{\partial v}{\partial z}\right)^2 + k^{33}_{001} \left(\frac{\partial w}{\partial z}\right)^2\Big] \Big\}$$
$$+ \frac{1}{8} \Big\{ k^{11}_{1'00}\Big[\left(a \frac{\partial u}{\partial x} + b \frac{\partial u}{\partial y}\right)^2 + \left(a \frac{\partial u}{\partial x} - b \frac{\partial u}{\partial y}\right)^2\Big] + k^{22}_{1'00}\Big[\left(a \frac{\partial v}{\partial x} + b \frac{\partial v}{\partial y}\right)^2 + \left(a \frac{\partial v}{\partial x} - b \frac{\partial v}{\partial y}\right)^2\Big] \Big\}$$

III-3

which may rewritten by collecting coefficients of the respective partial derivatives as:

$$u_I = a^2 \left(\frac{1}{2} k^{11}_{100} + \frac{1}{4} k^{11}_{1'00}\right) \left(\frac{\partial u}{\partial x}\right)^2 + \frac{1}{4} b^2 k^{11}_{1'00} \left(\frac{\partial u}{\partial y}\right)^2 + \frac{1}{2} c^2 k^{11}_{001} \left(\frac{\partial u}{\partial z}\right)^2$$
$$+ \frac{1}{4} a^2 k^{22}_{1'00} \left(\frac{\partial v}{\partial x}\right)^2 + b^2 \left(\frac{1}{2} k^{22}_{010} + \frac{1}{4} k^{22}_{1'00}\right) \left(\frac{\partial v}{\partial y}\right)^2 + \frac{1}{2} c^2 k^{22}_{001} \left(\frac{\partial v}{\partial z}\right)^2$$
$$+ \frac{1}{2} c^2 k^{33}_{001} \left(\frac{\partial w}{\partial z}\right)^2 \qquad \text{III-4}$$

To obtain an expression for the strain energy density, let us multiply both sides of the above by the number of units per cell and divide by the volume of the unit cell. From Figure 2.2, we have

$$\text{number of lattice units per cell} = 8\,(\tfrac{1}{8}) + 2\,(\tfrac{1}{2}) = 2 \qquad \text{III-5}$$

$$\text{volume of the unit cell} = abc\ .$$

Thus, the strain energy density U in terms of u_I may be written as:

$$U = \frac{2\,u_I}{abc} \qquad \text{III-6}$$

The corresponding expression from continuum theory is:

$$U = \frac{1}{2}(c_{11}\epsilon_1^2 + c_{22}\epsilon_2^2 + c_{33}\epsilon_3^2) + (c_{12}\epsilon_1\epsilon_2 + c_{13}\epsilon_1\epsilon_3 + c_{23}\epsilon_2\epsilon_3) + \frac{1}{2}(c_{44}\epsilon_4^2 + c_{55}\epsilon_5^2 + c_{66}\epsilon_6)^2$$

which, on substitution for the values of ϵ_j from 2.5 and 6, yields:

$$U = \frac{1}{2}\left[c_{11}\left(\frac{\partial u}{\partial x}\right)^2 + c_{22}\left(\frac{\partial v}{\partial y}\right)^2 + c_{33}\left(\frac{\partial w}{\partial z}\right)^2\right]$$
$$+ \left[c_{12}\left(\frac{\partial u}{\partial x}\right)\left(\frac{\partial v}{\partial y}\right) + c_{13}\left(\frac{\partial u}{\partial x}\right)\left(\frac{\partial w}{\partial z}\right) + c_{23}\left(\frac{\partial v}{\partial y}\right)\left(\frac{\partial w}{\partial z}\right)\right]$$
$$+ \frac{1}{2}\left[c_{44}\left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right)^2 + c_{55}\left(\frac{\partial w}{\partial x} + \frac{\partial u}{\partial z}\right)^2 + c_{66}\left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right)^2\right] \qquad \text{III-7}$$

Collecting coefficients, this may be rewritten as:

$$U = \frac{1}{2}c_{11}\left(\frac{\partial u}{\partial x}\right)^2 + \frac{1}{2}c_{66}\left(\frac{\partial u}{\partial y}\right)^2 + \frac{1}{2}c_{55}\left(\frac{\partial u}{\partial z}\right)^2 + \frac{1}{2}c_{66}\left(\frac{\partial v}{\partial x}\right)^2$$
$$+ \frac{1}{2}c_{22}\left(\frac{\partial v}{\partial y}\right)^2 + \frac{1}{2}c_{44}\left(\frac{\partial v}{\partial z}\right)^2$$
$$+ \frac{1}{2}c_{55}\left(\frac{\partial w}{\partial x}\right)^2 + \frac{1}{2}c_{44}\left(\frac{\partial w}{\partial y}\right)^2 + \frac{1}{2}c_{33}\left(\frac{\partial w}{\partial z}\right)^2$$
$$+ c_{12}\left(\frac{\partial u}{\partial x}\right)\left(\frac{\partial v}{\partial y}\right) + c_{13}\left(\frac{\partial u}{\partial x}\right)\left(\frac{\partial w}{\partial z}\right) + c_{23}\left(\frac{\partial v}{\partial y}\right)\left(\frac{\partial w}{\partial z}\right)$$
$$+ c_{44}\left(\frac{\partial v}{\partial z}\right)\left(\frac{\partial w}{\partial y}\right) + c_{55}\left(\frac{\partial w}{\partial x}\right)\left(\frac{\partial u}{\partial z}\right) + c_{66}\left(\frac{\partial v}{\partial x}\right)\left(\frac{\partial u}{\partial y}\right) \qquad \text{III-8}$$

Comparing III-4 and III-8 by using III-6, we obtain the following expressions for c_{ij} in terms of $k^{ij}_{\ell mn}$

$$c_{11} = \frac{a}{bc}\left(k^{11}_{100} + \frac{1}{2}k^{11}_{1'00}\right)$$

$$c_{22} = \frac{b}{ac}\left(k^{22}_{010} + \frac{1}{2}k^{22}_{1'00}\right)$$

$$c_{33} = \frac{c}{ab}\ k^{33}_{001}$$

$$c_{44} = \frac{c}{ab}\ k^{22}_{001} \quad \text{or } c_{44} = 0$$

$$c_{55} = \frac{c}{ab}\ k^{11}_{001} \quad \text{or } c_{55} = 0$$

$$c_{66} = \frac{1}{2}\ \frac{b}{ac}\ k^{11}_{1'00} = \frac{1}{2}\ \frac{a}{bc}\ k^{22}_{1'00}$$

$$c_{12} = 0$$

$$c_{13} = 0$$

$$c_{23} = 0 \quad . \qquad \text{III-9}$$

Except for c_{12}, c_{13} and c_{23} these are identical to the Expression 2.78. Even redundancy in expressions for c_{44}, c_{55} and c_{66} is same as before. This provides a check on the two procedures. Such an agreement will not, however, be obtained if non-central forces are considered because different higher order terms are neglected and included in the two cases.

APPENDIX IV

A NOTE ON THE LENNARD-JONES POTENTIAL

Intermolecular forces are approximated by a 6-12 Lennard-Jones potential,

$$\phi(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \qquad 2.26$$

or

$$\phi(r) = \epsilon \left[2 \left(\frac{r_{min}}{r}\right)^{12} - \left(\frac{r_{min}}{r}\right)^6 \right] . \qquad IV\text{-}1$$

Both of these forms are listed by Hirschfelder, et al (21). The first is used herein, and this is also the form employed by Born and Huang (23). However, Peterlin, et al (30), McMahon and McCllough (31) use variations of the second. Further, they employ one potential along the b-axis and another along the diagonal (a, b) axis, thus calculating different values of r_{min} along these directions. This is probably done because of the inherent properties of the orthorhombic lattice of polyethylene:

(i) There is an additional unit at the midpoint of the rectangle (a, b).

(ii) This unit is at a distance of $\frac{1}{2}\sqrt{a^2 + b^2}$, which is not equal to b.

(iii) The unit has an orientation different from the corner units.

Nevertheless, a closer study of the lattice structure of polyethylene reveals that such difficulties may be resolved without using different potential forms in different directions.

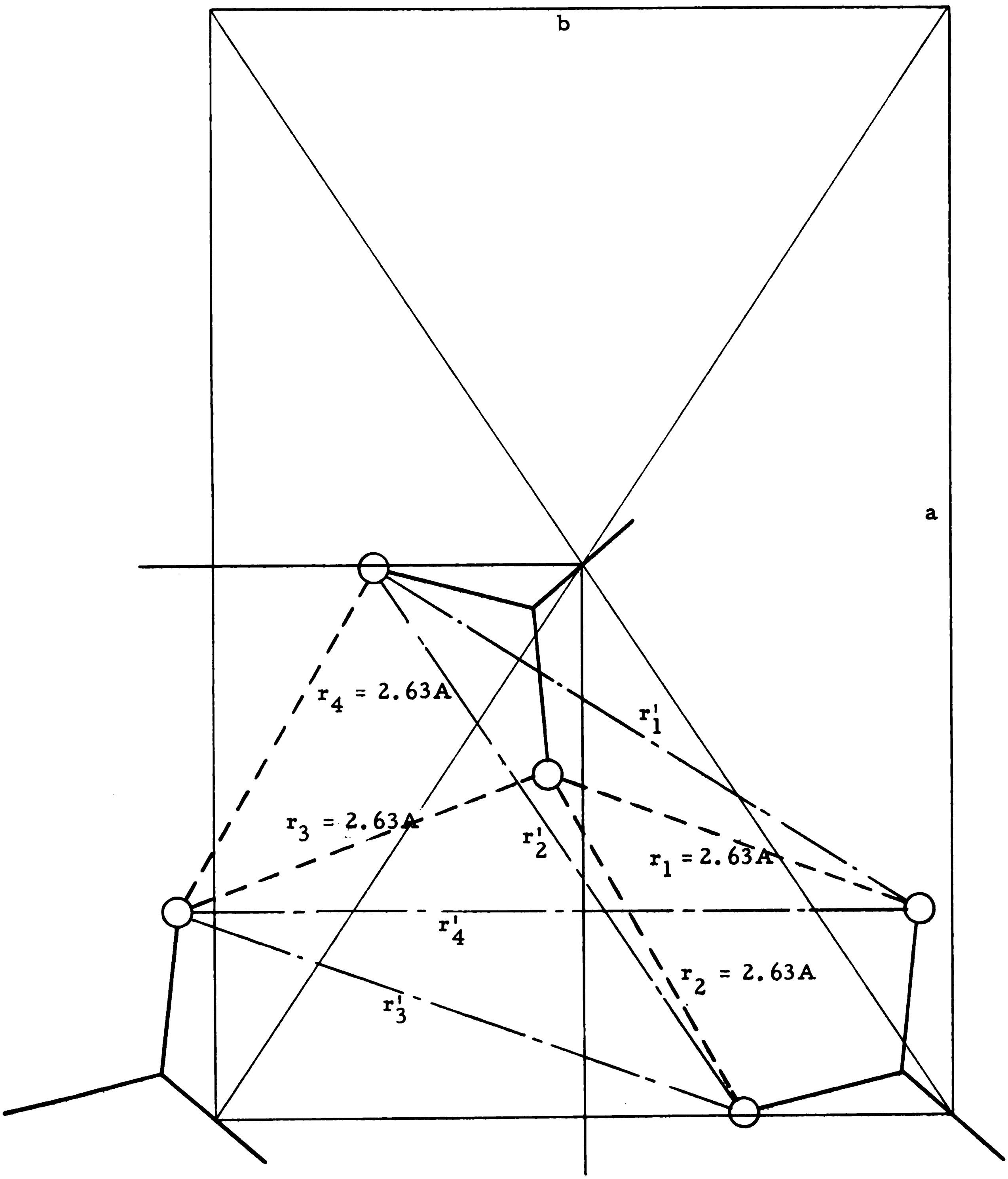


Figure IV-1. Detailed positions of the hydrogen atoms in the (a, b) plane.

Figure IV-1 is a detailed drawing of a single cell of polyethylene in the plane (a, b), showing the positions of the hydrogen atoms in space relative to each other. It may be observed from this figure that the separation distances r_1, r_2, r_3 and r_4 of the hydrogen atoms are all equal. This suggests that:

(i) The geometry of the polyethylene molecules and their location in space determine the lattice structure.

(ii) The London dispersion forces between hydrogen atoms determine the Lennard-Jones potential such that the hydrogen atoms are at equilibrium separation.

Thus, the net force between any two lattice units in a plane is a result of the interaction of their hydrogen atoms. The potential between the two nearest hydrogen atoms can be written as

$$\phi'(r) = \frac{A'}{r^{12}} - \frac{B'}{r^{6}} \qquad \text{IV-2}$$

where the ratio of A' and B' is determined by their equilibrium distance r_o'. The net potential ϕ between the two units at the lattice points is:

$$\begin{aligned}\phi(r) &= 2\left[\phi'(r_1) + \phi'(r_2) + \phi'(r_3) + \phi'(r_4)\right] \\ &\quad + 2\left[\phi'(r_1') + \phi'(r_2') + \phi'(r_3') + \phi'(r_4')\right] \\ &= 8\left[\phi'(r_o') + \phi'(r')\right] \qquad \text{IV-3}\end{aligned}$$

VI. BIBLIOGRAPHY

1. P. H. Lindenmeyer, J. Polymer Sci. Part C, Polymer Symposia, 1, 5 (1963).
2. R. L. Miller, L. E. Nielsen, J. Polymer Sci., 44, 391 (1960) and 55, 643 (1961).
3. P. H. Till, Jr., J. Polymer Sci., 24, 301 (1957).
4. A. Keller, Phil. Mag., 2, 1171 (1957).
5. E. W. Fischer, Z. Naturforsch., 12a, 753 (1957).
6. P. H. Geil, "Polymer Single Crystals," Wiley, New York, 1963.
7. P. H. Geil, "Growth and Perfection of Crystals," Editors: R. H. Doremus, B. W. Roberts and D. Turnbull, Wiley, New York, 1958.
8. D. C. Basset, A. Keller, S. Mittsuhashi, J. Polymer Sci., 1A, 763 (1963).
9. G. C. Claver, Jr., R. Buchdahl, R. L. Miller, J. Polymer Sci., 20, 202 (1956).
10. E. A. Cole, D. R. Holmes, J. Polymer Sci., 46, 245 (1960).
11. C. W. Bunn, Trans. Faraday Soc., 35, 482 (1939).
12. H. B. Huntington, "The Elastic Constants of Crystals," Academic Press, New York, 1958.
13. F. W. Billmeyer, Jr., "Textbook of Polymer Science," Wiley, New York, 1963.
14. Charles Kittel, "Introduction to Solid State Physics," Wiley, New York, 1962.
15. S. Mizushima, T. Simanouti, J. Am. Chem. Soc., 71, 1320 (1949).

16. P. A. Small, J. Appl. Chem., 3, 71 (1953).

17. T. Shimanouchi, H. Asahina, S. Enomoto, J. Polymer Sci., 59, 93 (1962).

18. W. J. Dulmage, L. E. Contois, J. Polymer Sci., 28, 275 (1958).

19. J. F. Nye, "Physical Properties of Crystals," Claredon Press, Oxford, 1957.

20. F. London, Trans. Faraday Soc., 33, Part 1, 8 (1937).

21. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, 1964.

22. C. K. Ingold, "Introduction to Structure in Organic Chemistry," G. Bell and Sons Ltd., London, 1956.

23. M. Born, K. Huang, "Dynamical Theory of Crystal Lattices," Oxford, 1954.

24. F. Seitz, "Modern Theory of Solids," McGraw-Hill, New York, 1940.

25. R. A. Buckingham, Proc. Roy. Soc. (London), A, 168, 264 (1938).

26. J. E. Jones (Lennard), A. E. Ingham, Proc. Roy. Soc. (London), A, 107, 636 (1925).

27. Dow Polyethylene R 301, Plastic Sales, The Dow Chemical Company, Midland, Michigan.

28. A. Muller, Proc. Roy. Soc. (London), A, 154, 624 (1936).

29. K. Knopp, "Infinite Sequences and Series," Dover, New York, 1956.

30. A. Peterlin, E. W. Fischer, Chr. Reinhold, J. Chem. Phys., 1403 (1962).

31. R. L. McCllough, P. E. McMahon, Trans. Faraday Soc., 60 (12), 2089 (1964).