

INTERMOLECULAR FORCES ^{IN} ~~OF~~ BOUNDARY FRICTION

by

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ABSTRACT

A Computer program was used to plot the orthorhombic structure of fatty acid crystals on a chosen set of axes to approximate to a dynamic model of boundary lubrication. By using the exact laws of repulsive and attractive interactions between molecules, changes of the magnitude of forces due to shear and compression can be calculated. The setting angle was derived for the system and by using different repulsion potentials under compression, the number of molecular layers can be gauged. Shear was developed using internal rotation, lifting and the inclination of the molecules to the vertical. By using statistics the effect of the polycrystalline structure of metals may be evaluated (this also shows the anisotropy of friction data with respect to different crystal planes). Coefficients of friction are of the correct order and the magnitude of the forces involved show the correct relationships to each other for several differing systems.

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TABLE OF CONTENTS

Title	1
Abstract	2
Acknowledgements	3
Table of Contents	4
Chapter 1	<u>INTRODUCTION AND THEORIES OF FRICTION</u>
1.1	Introduction 7
1.2	Regimes of Friction 7
1.3	Classical laws of Friction 7
1.4	Theoretical models of Friction 9
1.5	Energy dissipation in Friction processes 9
1.6	Theories of Boundary lubrication 11
1.7	Cameron's Theory of Boundary lubrication 13
1.8	Coefficient of Friction as a function of load 15
1.9	Conclusions 16
	References 17
Chapter 2	<u>DISCUSSION OF MODEL</u>
2.1	Properties of Metallic Surfaces 18
2.2	Crystal structures of paraffin and Fatty Acid lubricants. 18
2.3	Orientation of layers to Surface 19
2.4	Adsorption and formation of boundary layer 20
2.5	Appliability of Elasticity theory 23
2.6	Internal rotations in methyl radials 23
2.7	Conclusion 24
	References 26
Chapter 3	<u>INTERACTIONS OF ATOMS AND MOLECULES</u>
3.1	General discussion 27
3.2	Types of attractive forces and their occurrence 28
3.3	Interaction between condensed phases 31
3.4	Repulsive forces 31
3.5	Summation of forces 34
3.6	Suitability to model 34
3.7	Combinations of potential 35
3.8	Program of H-H interaction curve 35
	References 40

Chapter 4	<u>FUNCTION AND PARAMETERS OF MAIN PROGRAMS</u>	
4.1	Introduction	41
4.2	Lattice and chain Dimensions	41
4.3	The Summation Arrays	44
4.4	Z array, screening effects and weighing factors	47
4.5	Co-ordinates of H atoms in methylene groups	49
4.6	Co-ordinates of H atoms in methyl groups	49
4.7	CH and HH attractive potentials	49
4.8	HH Repulsive distances	50
4.9	Displacement Parameters	50
4.10	Setting Angle	51
4.11	Compression	51
4.12	Shifting from the Vertical axis	52
4.13	Parameters describing internal rotations	52
4.14	Programing Method	55
	References	55
Chapter 5	<u>CHECKING PROCEDURE</u>	
5.1	Boundary Conditions of Co-ordinate system	59
5.2	Boundary Conditions of rotations	60
5.3	Displacement and orientation over the cell	60
5.4	Checking with Cameron's Model	60
5.5	Program to Calculate Setting Angle	70
5.6	Results and Conclusions of Setting Angle program	72
5.7	Compression of crystals in XY direction	77
	References	82
Chapter 6	<u>COMPRESSIBILITIES</u>	
6.1	The Importance of Compressibility Data	83
6.2	Theory of elastic Compression	83
6.3	Applicability to Boundary layers	86
6.4	Relationship between layer number, Elasticity and Compression diagram	86
6.5	Anisotropic Compression of layers	87
6.6	Correlation of No. of layers with potential functions	91
6.7	Representation of Potentials	92
6.8	New potentials to describe monolayers	92
6.9	Introduction of Rock and Rot	95
6.10	Conclusions	95
	References	95

Chapter 7	<u>SHEARING OF THE MODEL</u>	
7.1	Shear across the X-AXIS	97
7.2	Effect of Rotation of end groups	97
7.3	Types of Friction	97
7.4	Statistics of Shear related to the X-AXIS	98
7.5	Investigation of Lifting with Shear	99
7.6	Statistics of Lifting	100
	References	100
Chapter 8	<u>RESULTS</u>	
8.1	Results using compressibility curves	116
8.2	Effect of other compressive distributions	120
8.3	Results using Shear, Rotations and Shift	120
Chapter 9	<u>DISCUSSION</u>	
9.1	Shear as a function of Rotations and Inclination	132
9.2	Compressibilities and Shear	132
9.3	Applicability of Potentials	133
9.4	Results as a function of layer height	133
9.5	Surface Roughness	133
9.6	Theories of Boundary Friction	134
9.7	Adhesion	134
9.8	Light Loads	134
9.9	Statistics of model, Physical and Chemical Adsorption	139
9.10	Model and parameters used in the program	139
9.11	Effect of the Solid Phase	140
	References	140
Chapter 10	<u>CONCLUSIONS AND FUTURE WORK</u>	
10.1	Conclusions	141
10.2	Improvements of the model and future work	141
<u>Appendix A</u>		
	Chain meshing under Compression	143
<u>Appendix B</u>		
	Infinite and finite layers	144
<u>Appendix C</u>		
	Main Subroutine of the main program	145

CHAPTER 1 - INTRODUCTION AND THEORIES OF FRICTION

1.1 Introduction

This chapter contains an introduction to the different types of friction and their explanation according to several authors. Energy dissipation and its relevance to molecular theories is discussed and a brief literature survey is included to cover all relevant points. The basic requirements of a boundary lubricating model are also discussed. Detailed points are sometimes deferred until the appropriate sections of later chapters to avoid repetition.

1.2 Regimes of Friction

The fundamental regime is dry friction. It exists between any two bodies in the absence of a third phase which could act as a lubricant. If a lubricant is introduced between the two bodies and a frictional force applied to cause motion, so that the lubricating layer obeys the hydrodynamic laws of laminar flow, then the regime is called hydrodynamic friction. The system obeys Newton's laws and its properties are a function of viscosity.

Under higher loads and at lower speeds a coherent film can no longer be maintained, contact of the surfaces occurs, even in the presence of the lubricant. This region is termed boundary lubrication and the effectiveness of boundary lubricants is governed by their ability to adsorb on the sliding surfaces and is independent of their viscosity.

There is a great deal of confusion regarding this definition and disagreement over the role of the lubricant. Boundary friction (or any type) is the statistical sum of thousands of interactions under many different conditions and cannot be thought of as a rigorously defined process. There are two intermediate regimes separating the three already discussed acting as transition regions.

1.3 Classical laws of Friction

The friction force is the statistical result of atomic interactions between two surfaces in relative motion. Irrespective of the type of friction these forces are resolved into elementary interaction between pairs of atoms. In reality, due to the rough metallic profile, the interaction surface is not continuous but composed of isolated interaction areas.

Under these conditions the 'nominal area' is greater than the true area. When the nominal area is increased the true area for rough surfaces will vary insignificantly, hence it follows that the

frictional forces are independent of the nominal area as observed by Coulomb.

The basic law governing frictional force and external load was formulated by Amonton, the two parameters being directly proportional to each other, the constant termed the Coefficient of Friction

$$\text{i.e. } F = \mu N \quad - (1)$$

Coulomb confirmed this work and introduced a constant term A to account for adhesive seizing of the surfaces.

$$\text{i.e. } F = \mu N + A \quad - (2)$$

Thus the Classical laws of friction (Dry and Lubricated) can be stated as

- (a) Frictional force directly proportional to the load
i.e. Coefficient of friction independent of load.
- (b) Force independent of area.
- (c) Force depends on the nature of the sliding surfaces.
- (d) Independent of sliding velocity.

The last point stems from the fact that traditionally friction was treated as a Mechanical force which has the property of being independent of velocity

In practice coefficients of friction have to be considered as functions of several variables i.e. pressure, surface roughness, velocity, temperature. If the conditions of the system are changed to increase the relative importance of one of these variables the Classical laws are broken. Investigation of the relative motion of lubricants using atomic laws should reveal trends when considering these parameters in turn.

Akhmatov states (1) that the mechanism of boundary friction is determined by many factors, including

- (a) Physical nature, state and properties of the solid surface.
- (b) Structure and properties of lubricant molecules.
- (c) Nature of adsorption of the molecules.
- (d) Parameters like pressure, thickness of layer, velocity, temperature.
- (e) Changes in Structure of boundary layer during friction.

The author also states (2) that

"The laws of Amontons and Coulomb belong to those statistical laws of nature in which the outward simplicity conceals a profound complexity of phenomena."

1.4 Theoretical models of Friction

There are several differing views concerning the nature of friction. The first group explains friction in terms of lifting microasperities over each other and ideas based on geometric considerations - it was thought that the coefficient of friction was given by the tangent of the angle of inclination of the asperities. *i.e.* Euler and today Bickermann & Gretz (3).

The second group attempts to explain friction as a result of overcoming the forces of molecular attraction between two solids - reflected in the work of Hardy (4), Tomlinson (5) and Deryagin (6). This group also contains Bowden and Tabor (7) who proposed that friction is the force required to overcome welded junctions formed between solids as a result of molecular interaction. It also includes Cameron (8) who was the first to try to explain boundary friction in terms of the shearing of boundary lubricants using exact intermolecular forces.

The third group visualises friction as arising from the deformation of the material penetrated by asperities. *i.e.* Leslie (1801) and more recently by Epifanov and Minaev (9) who interpreted friction as being due to shearing.

The fourth group consists of composite theories. The most interesting was proposed by Coulomb (1779) who considered friction as a combination of lifting and penetration of asperities.

The main scope of this work is an examination of Cameron's (8) work, an attempt to explain properties of lubricant layers in terms of the exact laws of Molecular Physics and drawing conclusions in the light of theories of boundary friction.

1.5 Energy dissipation in Friction processes.

Consider the perfect potential of a conservative force obeying Newton's law.

$$\text{i.e. force } \underline{F} = \frac{dp}{dt} \quad (\text{Rate of change of momentum})$$

$$\text{also } \underline{F} = - \frac{\partial V}{\partial x} \quad \text{where } V = \text{Potential} \quad - (3) \\ X = \text{distance}$$

Consider this perfect potential varying periodically *i.e.* a sinusoidal curve representing undamped simple harmonic Motion. If a particle is released from a position of unstable equilibrium there will be no energy losses. *i.e.* Conservation of Energy.

$$T + V = \text{constant}$$

$$T = \text{Kinetic Energy}$$

$$V = \text{Potential Energy}$$

Controversy has surrounded these ideas ever since Coulomb proposed his ideas of friction based on the engagement of surface asperities and the coefficient of friction being the maximum slope of the asperities.

Leslie raised objections, as he maintained the theory could not explain any loss of energy in sliding, due to the periodic rise and fall of the masses in motion. Leslie's objections have been countered by Bikerman and Gretz (3) who explained Coulomb's idea in terms of thermo-dynamics i.e. Leslie's argument would be valid if the system is isothermal and reversible (Quasi-static and infinitely slow) but if the load is allowed to fall from the top of an asperity this represents an irreversible process.

Bikerman's argument has been in turn countered by Tabor (10) in his explanation of the Adhesion Theory, which considers friction to be caused ultimately by shearing of surface forces. Here the same problems of periodic potentials arise but the situation is quite different. According to the author

i.e. (a) Bikerman's concepts do not apply on a Micro scale

(b) Without detailed analysis thermo dynamics cannot readily be applied to the strength properties of solids.

"it cannot be applied to sliding or shear which involves large displacements on the atomic scale. As one plane is moved over the other, the interatomic bonds are stretched and the lattice is distorted elastically. At some critical stress the bonds are finally broken; the strain energy is then dissipated as vibrations in the lattice and this energy can never be recovered by subsequent reformation of the next series of bonds. The process is basically non conservative. The making and breaking of bonds in a solid by shearing is fundamentally a dissipative process."

i.e. $F = -\frac{\gamma}{x} + F^1$

Force is non conservative.

Deryagin's (11) theory of Boundary lubrication starts from the model of two identically orientated rows of molecules in intimate contact sliding upon each other. The atomic structure of their crystal planes determinesthe structure of their molecular fields. The author assumed the configuration of equipotential surfaces of such fields to be a system of mutually tangential spherical surfaces of equal radii. It is also assumed that the external pressure brings about repulsive forces by crowding the electron clouds of the atoms.

"Under such conditions the relative slipping should involve an expenditure of work and consequently forces of resistance to slipping should appear."

Both Tabor and Deryagin assume the dissipation of energy when relative motion takes place between two surfaces because there is a continuous change in the molecular pairs balancing the load.

This concept was also used by Cameron (8) see section 1.7. The work presented in later chapters uses the same assumptions inherent in all molecular theories. All the changes of energy associated with molecular pairings balancing the load are considered dissipated and by the absolute nature of the assumption all conclusions drawn must have the same maximum nature.

1.6 Theories of Boundary lubrication

Deryagin (6) developed a molecular theory in which account was taken of both repulsive and attractive molecular forces. The idea was that friction between smooth surfaces resulted from 'molecular roughness' due to repulsive forces. Adhesional forces, accounted by attractive forces, were introduced as a corrective term to describe departures from the Amonton law. This theory leads to a two termed equation relating the force of friction F and the normal load N .

$$\text{i.e. } F = \mu_0 S (p_0 + p) \quad - (4)$$

μ_0 = 'true coefficient of friction'. (Deryagin)

S = area of true contact

p_0 = specific force of molecular interaction

p = specific external pressure $N = Sp$.

The main feature of the equation implies a force of friction F_0 when the load N is zero.

$$\text{i.e. } F = F_0 + \mu_0 N$$

(Where μ_0 is the gradient of the straight line.) Denisov (12) checked equation (4) for paraffins and fatty acids as a function of layer thickness. Fig 1 (1) shows a set of these curves for myristic acid.

Another theory of Boundary lubrication is linked with Bowden and Tabor's Adhesion theory, see fig 1 (2). The force of dry friction is equated to the shearing of a material of mean shear strength. Thus we may write $F = As$, where A is the real contact area. As A is directly proportional to the load it follows that

$$\mu = \frac{F}{N} = \frac{As}{Ap} = \frac{s}{p} = \frac{\text{shear strength}}{\text{yield pressure}} \quad - (5)$$

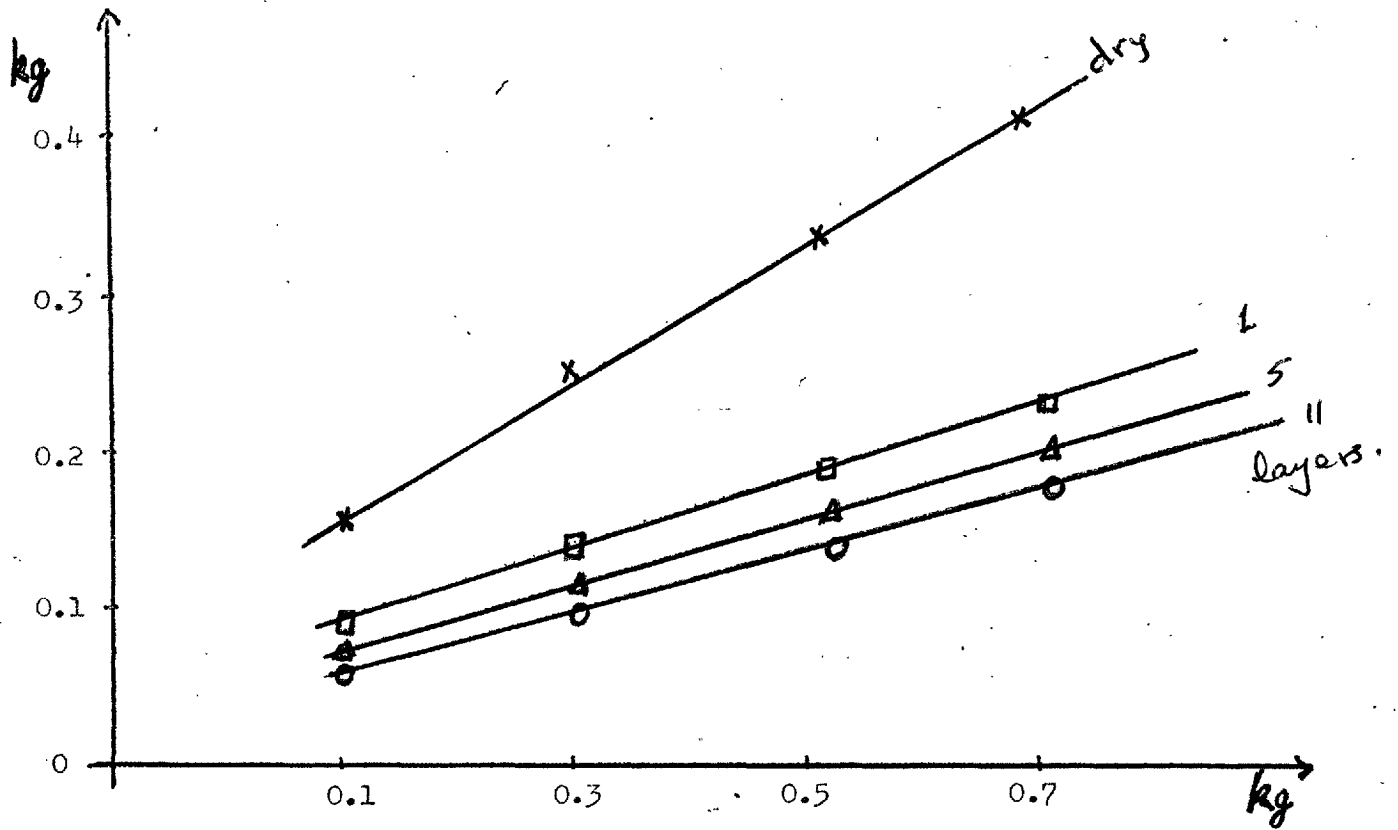


Fig. 1 (1) Curves of Friction against Load for Myristic Acid of different thickness. X = dry Friction, $\square$, Δ , $\circ$ respectively mono, five, and eleven molecular layers.

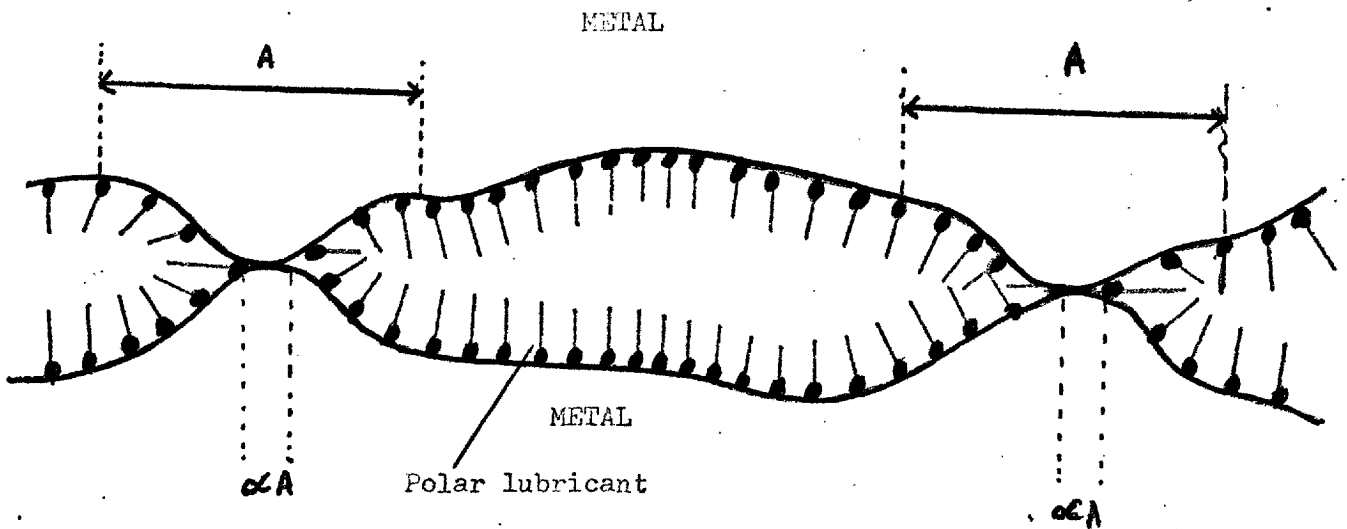


Fig. 1 (2) Bowden - Tabor scheme of Boundary Lubrication.

By an analogous argument and reference to fig 1 (2) the Boundary frictional force may be expressed as the sum of two terms. (i) The force $\alpha A s$ required to shear the metallic junctions (α is fraction of area over which metallic junctions are formed) (ii) force to shear the lubricant film $A (1 - \alpha) S_l$

$$F = A (\alpha S + (1 - \alpha) S_l). \quad - (5)$$

Thus if α is constant, F is proportional to A and Amontons law will hold, see equation (4). Tabor (13) concluded that α is of the order of 2 or 3%, and with good lubricants the major part of the resistance to sliding comes from shearing of the lubricant film.

Several objections to this theory can be found in the literature, Akhmatov (14), Toporov (15). More theories and their counter arguments exist and several schools of thought all emphasize different aspects when dealing with Boundary lubrication. While there are no irreconcilable contradictions the most basic approach to understanding the problem consists of studying the atomic and molecular interactions present in boundary layers.

1.7 Cameron's Theory of Boundary Lubrication

Cameron (16) was the first to consider a system of crystal planes, using X-ray information by Müller (see Chapters 2 and 3), and trying to calculate interaction forces between a chosen molecule and the adjacent layer as a function of pressure.

Ideal smooth surfaces were assumed without roughness or with their asperities squeezed flat by plastic deformation. "Let E_1 be the potential energy of one chain attached to one surface with respect to all the other chains on the other surface, at equilibrium. This is taken to be the same as the potential energy of a chain in one layer of molecules in a hydrocarbon crystal with respect to all the other chains one level down. When one surface is moved from the stable equilibrium position to the next equilibrium point, there must be one point between these two positions where the total attraction energy is a minimum. Let energy at this point be E_2 then if the distance between the two positions associated with the energies E_1 and E_2 is X ; the mean force F needed to move one chain from the position corresponding to E_1 to that corresponding to E_2 is

$$E_1 - E_2 = FX "$$

Knowing the cross sectional area of one chain and the distance X the force/cm² associated with a particular pressure can be calculated.

Because of the tedious nature of calculating the Van der Waals

attractive potential by hand Cameron made many wrong assumptions concerning E_2 , repulsive potentials, and compressibilities. These objections and others in relation to the model chosen are listed below.

- (a) Cameron considered only non-polar paraffins and used methylene end groups instead of methyl groups, thus neglecting an all important hydrogen atom.
- (b) E_2 was assumed to tend to zero. As mentioned above, this was entirely due to the tedious nature of the calculation, but in this sense the model is not dynamic.
- (c) The compressibilities used for monolayers were assumed to be the same as the gap compressibilities in the lateral planes i.e. $E_c = E_{ab}$.

Many objections to the interpretation of the results have been cited, Akhmatov (17), Van Battum and Broeder (18).

There is one interesting suggestion from the latter authors, see fig. 1 (3). The diagram represents two compressed states D (0) and D (X), the former at the equilibrium position of the system and the latter a compression curve at a distance X from the first. The authors maintain the frictional energy barrier to be the sum of two parts (a) The Interaction energy between states A and A (X), parallel tangents and hence comparable states of compression i.e. $(E_1 - E_2)$, (b) the work done against the external load if the distance between the planes is increased from A to A (X).

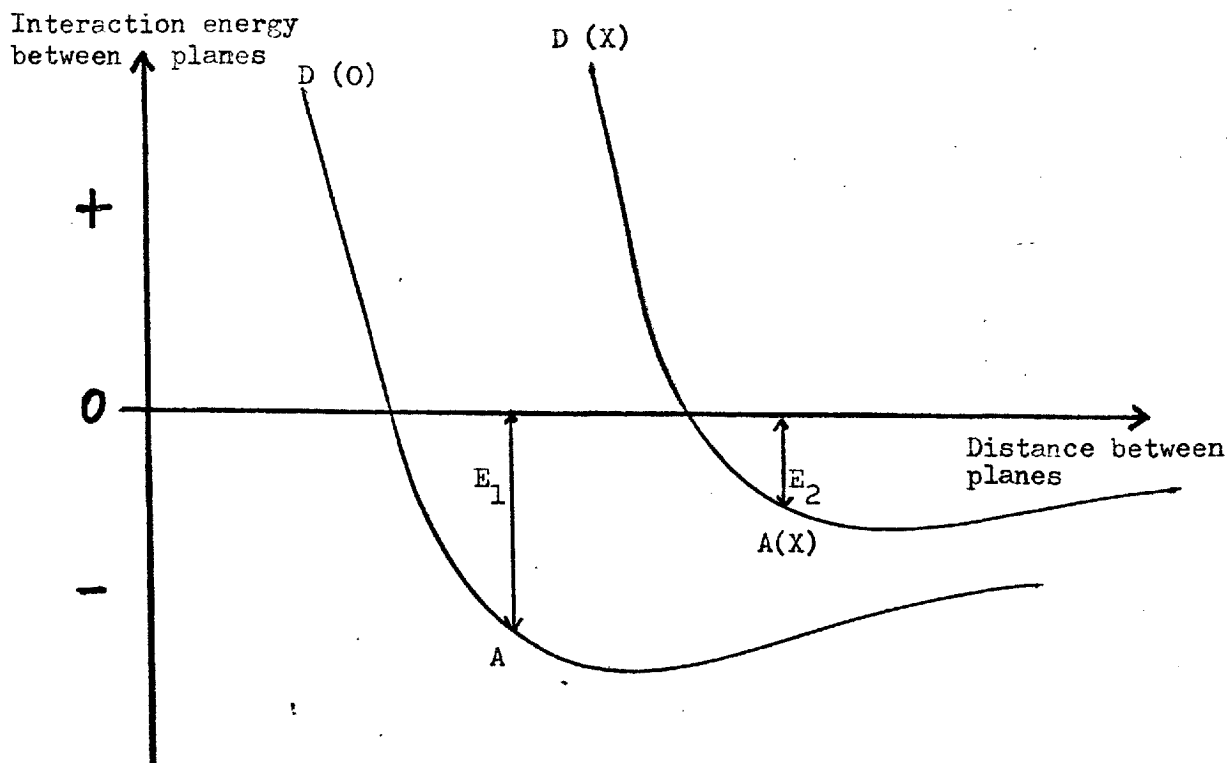


Fig. 1 (3) Compression diagrams at the equilibrium position D (0) and at a distance X from the first.

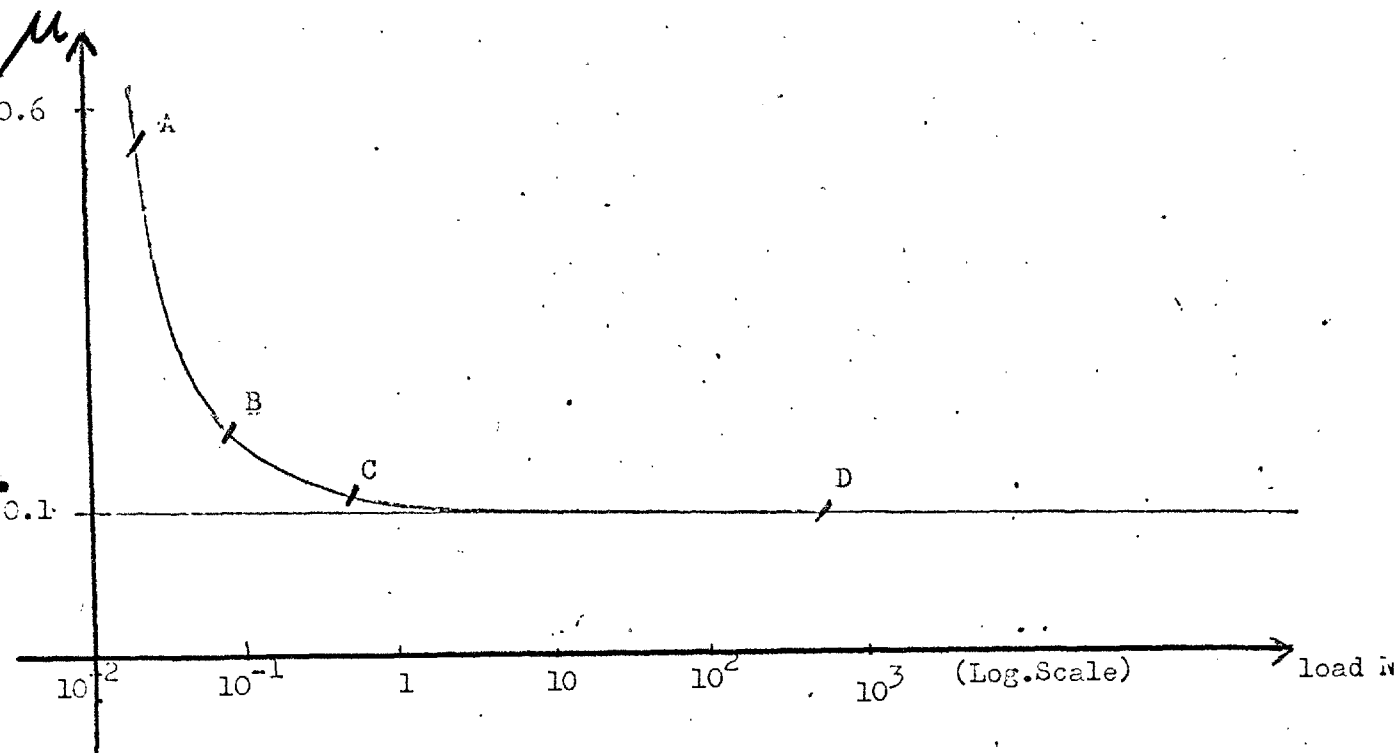


Fig. 1 (4) Variation with load of the coefficient of friction

1.8 Coefficient of Friction as a function of load

Several authors, Hardy (4), Whitehead (19), Kragelskii (20) point out the anomalous nature of equations (1) and (2) at light loads; fig. 1 (4). According to Hardy, section AB refers to a multimolecular boundary layer which has lost its fluidity, characteristic of the lubricant in bulk. As the pressure is increased, the layer thickness is reduced by the squeezing out of the lubricant - and friction increases.

Cameron maintains that fig. 1 (4) can be explained by equation (4)

$$\text{i.e. } F = F_0 + \alpha N$$

where α is the gradient of the straight line. The Coefficient of friction is defined as F/N therefore it follows

$$\mu = \frac{F}{N} = \frac{(F_0 + \alpha N)}{N} = \frac{F_0}{N} + \alpha \quad - (6)$$

If (6) is plotted and F_0 is small enough in comparison with N then when $N \gg F_0$, μ will tend to α . Also it follows that $\mu = \infty$ at $N = 0$ from this argument.

Kragelskii (20) uses a similar argument to Hardy's. i.e. As the load increases the film thickness decreases and thin lubricant films exhibit a greater resistance to shear, hence the frictional force increases but less rapidly than the increase in load. Fig. 1 (1) is used to corroborate this argument but in trying to explain fig. 1 (4) quantitatively, equation (5) is used which precludes the existence of F_0 .

$$\text{i.e. } F = \tau Ar$$

$$\text{where } \tau = (\alpha + \beta q) Ar$$

α = constant, depending on the sliding speed

q = pressure

β = general constant.

And $Ar = k N^X$ i.e. the increase of the real contact area takes place more slowly (in all cases except that of ideal plasticity) than the increase in load. (X varies from 1 to 0.6). Thus using $N = q Ar$.

$$\mu = \frac{F}{N} = \frac{\alpha k}{N^{1-X}} + \beta \quad - (7)$$

i.e. the coefficient of friction tends toward a limiting value.

Bowden and Tabor explain fig. 1 (4) in terms of their theory of Boundary lubrication (fig 1 (2) and equation (5)) by suggesting that at light loads there is no appreciable break through by the solid phase and the friction force (portion AB) represents the interaction of the film with itself. The area of shearing is no longer proportional to load, therefore μ rises. At higher loads the weight is supported by metal and the role of the lubricant is to reduce the metallic contact. Presumably at light loads by this theory the polar molecules are vertically orientated.

In contrast Adamson (21) maintains that figure 1 (2) represents the situation at very light loads and at normal loads the long chain lubricants separate the metals by lying flat.

Again in contrast, Deryagin does not mention any deviation from Coulomb's law at light loads unless the explanation is implicit in equation (4), in an analagous argument to Cameron's. Likewise no non-Russian authors seem to recognise Deryagin's two term law or diagrams such as fig. 1 (1).

1.9 Conclusion

This chapter demonstrates the differences between the major theories of friction and the differences in interpretation of Boundary Friction, especially in relation to light loads. The next Chapter shows the type of model assumed (broadly based on Cameron's ideas and work) and how it can be applied in its limit to give trends as functions of important parameters.

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CHAPTER 2 - DISCUSSION OF MODEL

2.1 Properties of Metallic Surfaces

If an ideal three phase frictional system is considered the metal will account for two of the phases. The properties of the metallic surface separate the three phases and hence will have a dominant effect on boundary lubrication. Several two and three dimensional statistical theories of surfaces exist (1) and Fourier analysis (2) has been used.

A number of theories of boundary friction consider the metallic surface to be ideally flat or plasticised flat by pressure c.f. Cameron. These theories obviously ignore the properties of real metals i.e. the profile, crystal structure, flaws and cracks. While it is desirable to include and take account of all these real properties an ideal theory must be adopted then adapted to encompass as many deviations as possible i.e. the theory must proceed step by step from an ideal situation to a real one.

The main property of real metals is that they are polycrystalline, thus any polar lubricant will have orientations depending on the orientation of the crystallites of the metal. In later chapters polycrystalline surfaces are approximated to by taking a statistical average of shear properties as a function of angle and distance from a fixed origin.

2.2 Crystal structure of Paraffin and Fatty Acid lubricants

A considerable amount of work was done by Muller (3) in determining the physical parameters of paraffin crystals and how they are packed in space. At equilibrium the structure must be consistent with the theory of Close Packing to achieve the minimum energy of the system, Kitaigorodskii (4).

Several crystal structures of paraffins are possible, orthorhombic; monoclinic; triclinic which depend on the degree of inclination from the vertical and even or odd number of carbon atoms.

The nearest derivative to paraffins are fatty acids which have similar crystal structures if the chains are sufficiently long, because packing is mainly due to the distribution of matter in the chains and the effect of the end groups is limited.

Akhmatov shows (5) that the structure of stearic acid is analagous to the structure of the corresponding paraffin. Several structures of crystals inclined to the vertical are shown but experimental data on the structure of fatty acid are very scarce. Consequently Muller's information on the paraffin $C_{29}H_{60}$ and Smith's parameters (6) on normal paraffins $C_{21}H_{44}$ to $C_{29}H_{60}$ are used to program a

layer of fatty acid (by including a methyl end group for a methylene group), see Chapter 4 fig. 4 (1).

2.3 Orientation of Layers to Surfaces

Tabor (7) maintains that the first layer is orientated vertically to the metal and other layers are orientated at an angle to the first. Godfrey (8) states that polar molecules, particularly long hydrocarbons adsorb with preferred vertical orientation. The chemisorption of stearic acid on oxidized steel surfaces to form a monolayer of iron stearate is shown in fig 2 (1). Kragelskii (9) states that the first layer is orientated differently from other layers and that normal and tangential orientation are possible. The former is typical of fatty acids in which there are different groups of atoms at each end.

From Müller's work the cross sectional area of a fatty acid chain is established at $18-20 \text{ \AA}^2$ and Zisman (10) showed that the point at which the coefficient of friction stops falling off linearly as the

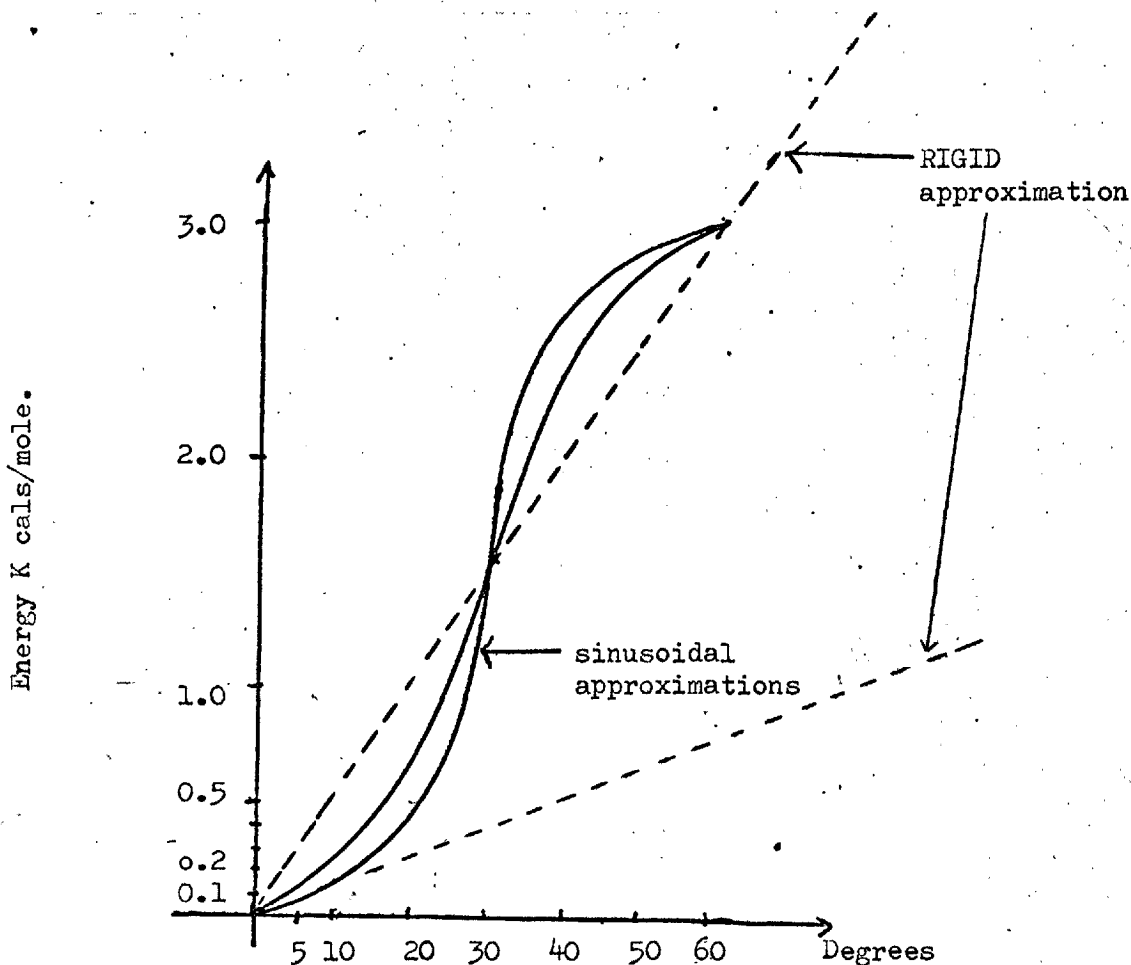


Fig. 2 (3) Graph of Energy against degrees for internal rotations of hydrogen atoms in methyl groups.

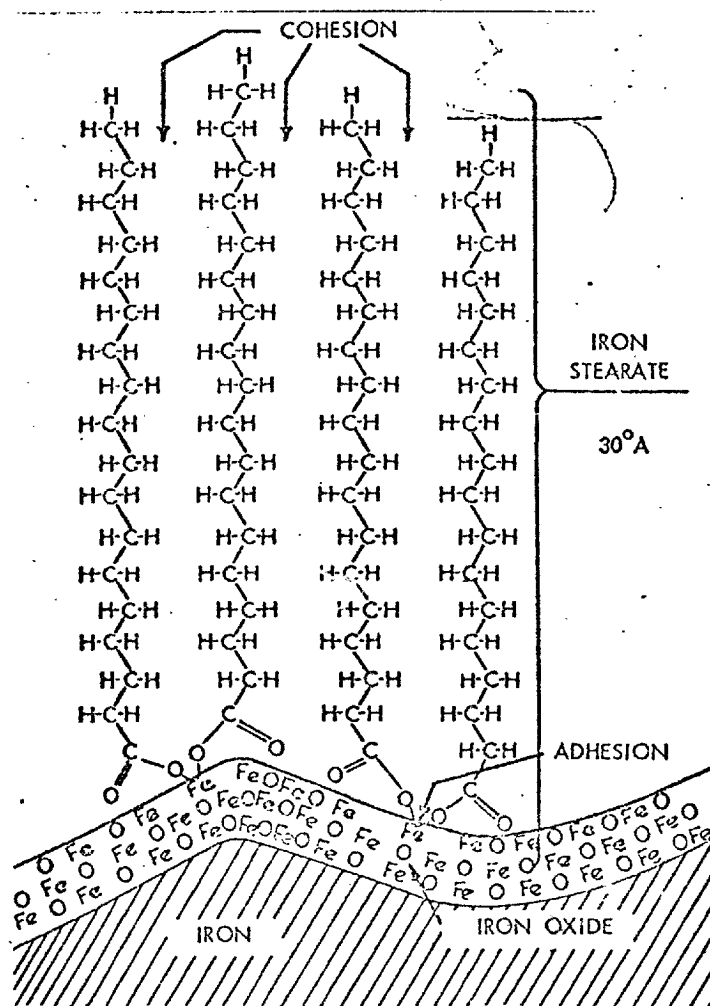


Fig. 2 (1) Schematic diagram representing the chemisorption of stearic acid on an iron surface to form a monolayer of iron stearate.

homologous series of fatty acids is ascended is consistent with solid characteristics of the acids i.e. surface area 20 Å^2 .

The general consensus of opinion is that fatty acids are orientated vertically in a monolayer then orientated subsequently at an angle to the vertical. This situation was reproduced in the computer programs.

2.4 Adsorption and formation of a boundary layer

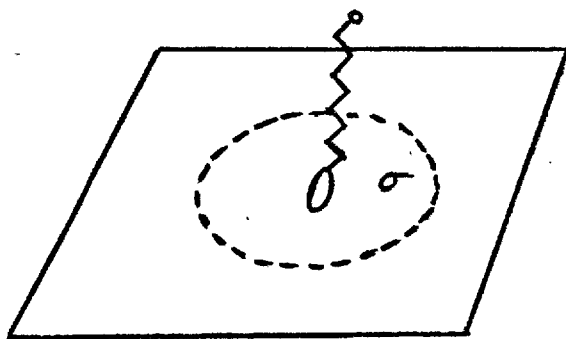
One theory of the formation of monolayers and multimolecular layers is dealt with by Akhmatov (11). It briefly assumes the formation of dimers, which are two polar molecules with the polar groups head on under the influence of orientation forces (see Chapter 3) and hydrogen bonds, of total strength approximately 15 kcal/mole . Single chains are also assumed to be present which are adsorbed to

the metal by virtue that their interaction energy is higher than the dimers. The adsorption forces are given as 13 kcal/mole. Hence it follows that only odd numbered layers are possible i.e. monolayers, then 3 layers, consisting of one dimer sandwiched between the monolayer with three methyl planes. A 'pack of cards' model is sometimes assumed when the system is subjected to tangential forces but a non isotropic profile of pressure can be assumed across the lubricant which implies slip about the symmetry plane. Combined interaction forces are of the order of 10^{-1} — 3 kcal/mole. The co-valent forces acting between the carbon atoms of the chain are of the order of 80 kcal/mole.

Another theory is advocated by Bowden and Tabor, (12) see fig. 2 (1) which assumes the formation of a surface soap caused by the reaction of the metal and the lubricant by chemisorption.

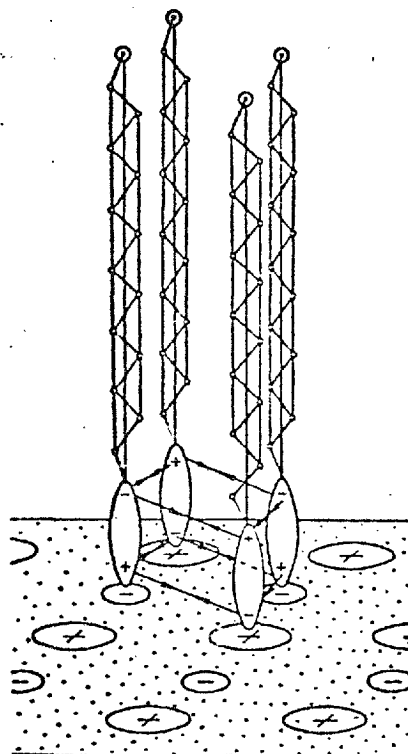
If the metal surface is represented by the Herzfeld model (alternate positive and negative charged sections) the formation of a saturated monomolecular layer can be represented in Fig. 2 (2). The polar groups are bound by Van der Waal's orientation forces.

The question of mobility of the adsorbed molecules has long been under review. If the molecule is chemisorbed to form a metallic soap because of the formation of a new layer, migration must seem very doubtful and the degree of freedoms of molecular thermal motion must be reduced. But in the case of physical adsorption migration and motion of molecules has long been recognised. According to Frenkel (13) the cross-sectional area of the active group of an adsorbed molecule is much less ^{THAN} the equipotential region of the neighbouring micro-field. A summary of evidence for surface migration by polar molecule is given by Akhmatov (14).

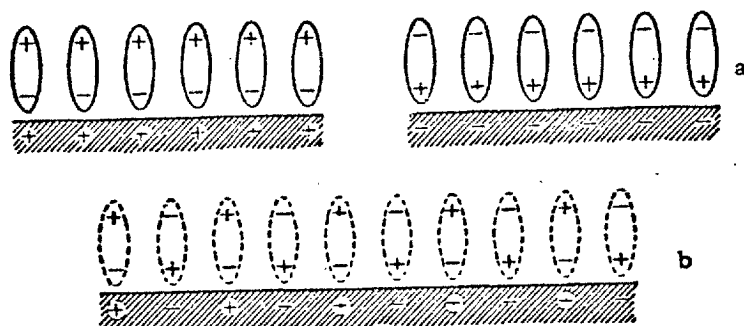


A polar molecule adsorbed on a metal surface can undergo displacements within the limits of the equipotential area

Fig. 2 (2) - Physical adsorption.



Four molecules of the fatty acid $\text{CH}_3 - (\text{CH}_2)_{13} - \text{COOH}$ physically adsorbed by orientation forces forming a saturated monomolecular layer.



- (a) Dipole orientation on positively and negatively charged surfaces.
- (b) Metal Surface.

2.5 Applicability of Elasticity theory

Three types of elasticity of boundary layers are of special interest (a) shear (b) Compression and tension in the Z direction (c) Compression in the XY directions. A dynamic theory of boundary layer can only equate the kinetic friction c.f. kinetic coefficient of friction, with the statistical result of breaking and forming of molecular bonds. Static friction, Akhmatov (15) is defined at the instant of transition to sliding after initial elastic then plastic movements. An explanation of this difference in terms of the model will be given in later chapters.

The question of compression and the applicability of Hooke's law and elastic constant is dealt with in Chapter 6, where assumptions of the degree of isotropy of these parameters with respect to the Z axis are made.

2.6 Internal rotations in Methyl radicals

Hydrocarbons and their derivatives form very long molecular chains and their length is limited only by their stability to thermal motion and velocity gradients. While still retaining the tetrahedral angle between the C-C bonds several basic isomers of hydrocarbon chains are possible, each having different energies. The most stable configuration, having the lowest potential energy is a simple meandric flat-trans isomer which occurs in Müller's model of paraffin and fatty acid crystals; fig. 4 (2). Akhmatov (16) quotes a figure of 0.5 kcal/mole to rotate a C-C valence bond through 1°. It is shown in section 5.6 that free rotation of chain in crystals is very rare and that the chains have the properties of a rigid body.

There has been a large amount of research Pitzer (17), Oosterhoff (18) Mizushima (19) in potential energy changes associated with rotation about single bonds. The problem involves a calculation of the quantum energy levels of the system, but the usual way is to assume a potential function and then calculate the energy levels.

A frequently used potential is of the form of

$$V = \frac{1}{2} V_0 (1 - \cos n\phi)$$

Where V_0 is the height of the potential peaks above the valleys, ϕ is the rotation angle, and n is the number of peaks per revolution. In the case of hydrocarbons in particular ethane and methyl radicals, n equals 3 from symmetry considerations.

$$\text{i.e. } V = \frac{1}{2} V_0 (1 - \cos 3\phi)$$

From the literature already cited the potential barrier is given as 3.0 ± 0.1 kcal/mole. Pitzer (17). If the peaks of the potential are then taken at 60°, 180°, 300° and a linear graph drawn between the

maximum and the minimum a rotation through 20, 10, 5 degrees respectively will take 1, 0.5, 0.25 kcal/mole. If a sinusoidal curve is approximated to, the energies involved will be 0.5, 0.2 and 0.1 kcal/mole approximately. Fig. 2(3). In the model the chains were taken as rigid and internal rotations of the end groups were introduced by the parameters ROCK and ROT.

2.7 Conclusion

The model which will be used in this work may be summarised as follows:

- a) A three phase system of metal, fatty acid and metal is assumed with the slip plane in the symmetry plane, due to an anisotropic compression profile in the Z direction.
- b) An orthorhombic crystal packing structure is assumed with lattice constants as given by Müller.
- c) The monolayer is orientated vertically and other layers slightly tilted.
- d) Eventually a polycrystalline surface is approximated to by taking the statistical average over distance and angle i.e. random orientation of the lubricant is taken with respect to the shearing direction.
- e) The possibility of internal rotations of the methyl group is assumed but chain deformations, twisting and bending, are secondary effects.
- f) Elastic constants are used for compression but the statistical result of gliding is taken to be analagous to kinetic friction.
- g) The layer is comprised of dimers which act as rigid bodies due to the high energies involved compared to shearing along the methyl plane.
- h) The effect of the solid phase is discussed and used in conjunction with the results obtained.
- i) The types of forces and potentials present in the system are discussed and represented in terms of Compressive data and multi-layers.
- j) Cameron's basic method of calculation is used i.e. expressing the energy present in any process in terms of a long chain molecule, then using the area to obtain a specific force.
- k) All the energy in shearing is assumed to be dissipated, including contributions of lifting and internal rotations.
- l) Both point centres of forces and scattering centres as determined by X-ray diffraction are used in all calculation.

It has been demonstrated that this model is idealistic but by proceeding in steps then adding refinements approximating to reality definite trends of behaviour and explanations of the role of a lubricant

film can be achieved, i.e. Akhmatov states (20) "For the theory of boundary friction a dynamic model of boundary layers would be an important contribution. This would first involve a calculation of the change in interaction energy of boundary layers during their relative motion along the X-axis. "

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CHAPTER 3 - INTERACTIONS OF ATOMS AND MOLECULES

3.1 General Discussion

To be in a position to explain the properties of a boundary layer one must first understand the laws governing the interaction of atoms and molecules which constitute such a layer. From electrostatic theory the potential of a system of point charges is

$$V = \sum_{j=1}^n \frac{e_j}{r_j} \quad - (1)$$

where n is the total number of charges, e_j is the magnitude of the j -th charge and r_j is the distance between the charge e_j and the source point.

The potential energy of a system of charges in the field of another system can be expressed in the expansion of the function $U = \phi(1/r)$

$$\text{i.e. } U = \frac{C_1}{r} + \frac{C_2}{r^2} + \frac{C_3}{r^3} + \dots + \frac{C_n}{r^n} \quad - (2)$$

Where C_n is the coefficient of the n -th term which depends on the properties of the charges and the co-ordinates of the system.

Again using electrostatic theory the first derivative of the energy with respect to the co-ordinate system yields the magnitude of the force

$$\underline{F} = -\text{grad } U \quad \text{or} \quad \underline{F} = -\frac{\partial U}{\partial r} \quad - (3)$$

Therefore from (2) it follows that all the force terms would be single valued, which does not comply with our experience of bodies resisting compression and extension.

It is usual to call the repulsive forces which resist compression positive and the attractive forces which resist extension negative. This implies that in the absence of external forces i.e. in the equilibrium state, the two types of forces must balance each other and have a resultant of zero. Alternatively at equilibrium the interaction curve (the sum of the repulsive and attractive terms) must have a turning point.

By considering equations (1), (2) and (3) it is also evident that the rates of change of the two types of forces with respect to distance must also be different. In compression the repulsive terms must increase more rapidly than the attractive terms, similarly if the body is subjected to extension the repulsive contribution must decrease more rapidly.

The following conclusions may then be made in relation to equation (3)

- (a) the series must have alternating signs.
- (b) the attractive terms must have lower powers than the repulsive terms.

As is well known the accuracy of any series approximation increases with the number of terms employed but in practice the accuracy of experimental data on crystal properties has to be taken into account which limits the number of terms.

Therefore in general the laws of interaction between two particles can be summarised as

$$U = \frac{-A}{r^m} + \frac{B}{r^n} \quad - (4)$$

All the information contained in this equation is shown in figures 3 (1) and 3 (2).

3.2 Types of Attractive force and their occurrence

In the discussion of attractive forces or long range forces as they are conveniently called, it is customary to consider four classes.

- (a) Electrostatic
- (b) Induction
- (c) Dispersion
- (d) Resonance

The force between two non-polar molecules, which have no resultant angular momentum are of the dispersive type (so called because of some parallels to the theory of light). When a non-polar molecule interacts with a polar molecule both dispersion and induction forces occur. When two polar molecules collide - electrostatic forces come into play.

The electrostatic and induction forces can be understood classically and are in fact First Order Perturbations. Dispersion and Resonance forces are purely Quantum Mechanical and are Second Order Perturbations.

The attractive forces between systems of electric charges which are as a whole neutral are called Van der Waals forces (so named because they help to explain the deviations from the Perfect gas law first pointed out by Van der Waal). As a whole they possess certain properties

- (a) they are universal for such system.
- (b) Single valued - implying attraction.
- (c) Operate over relatively large distances.

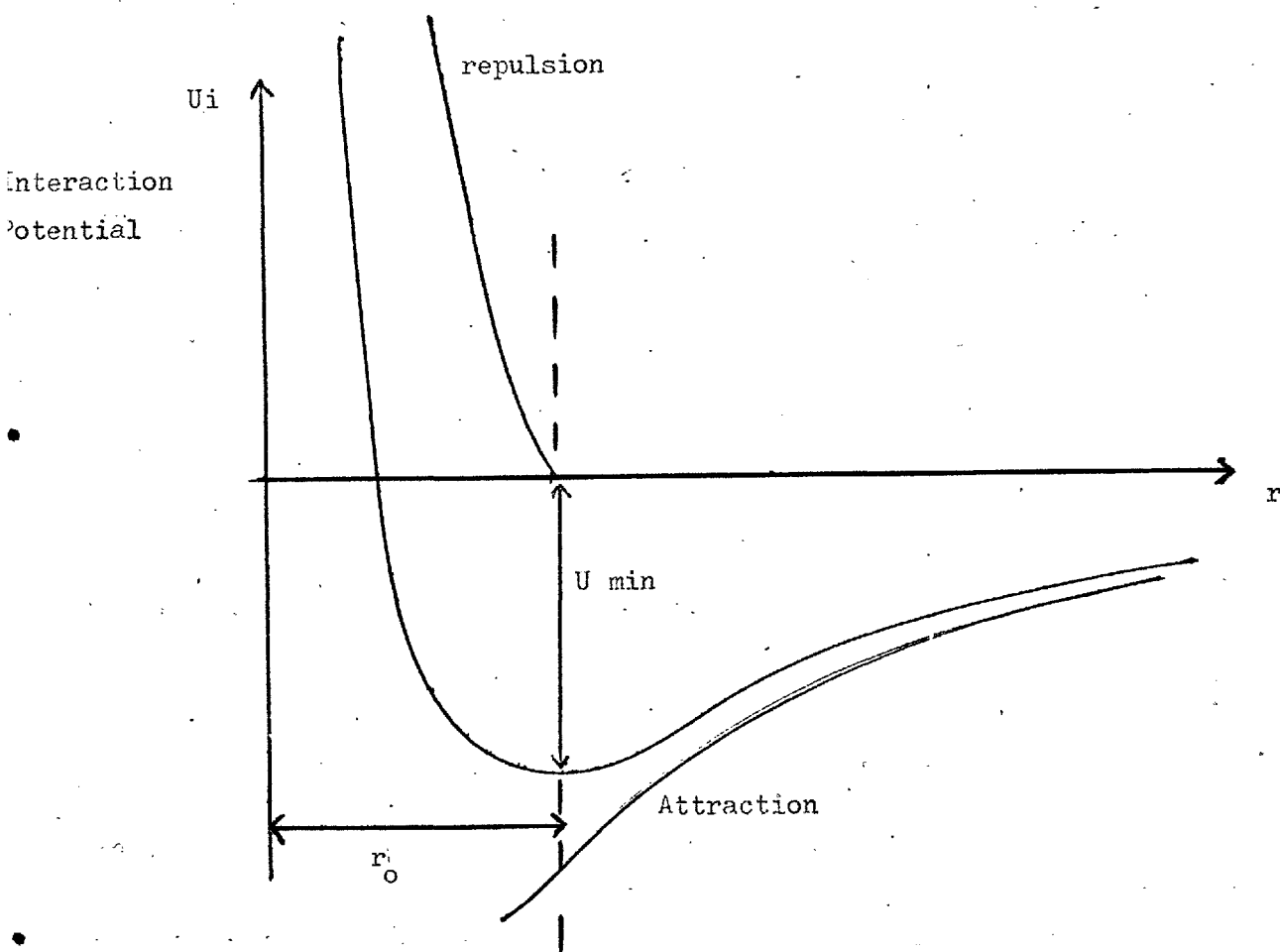


Fig. 3 (1) Potential energy as a function of distance between two particles.

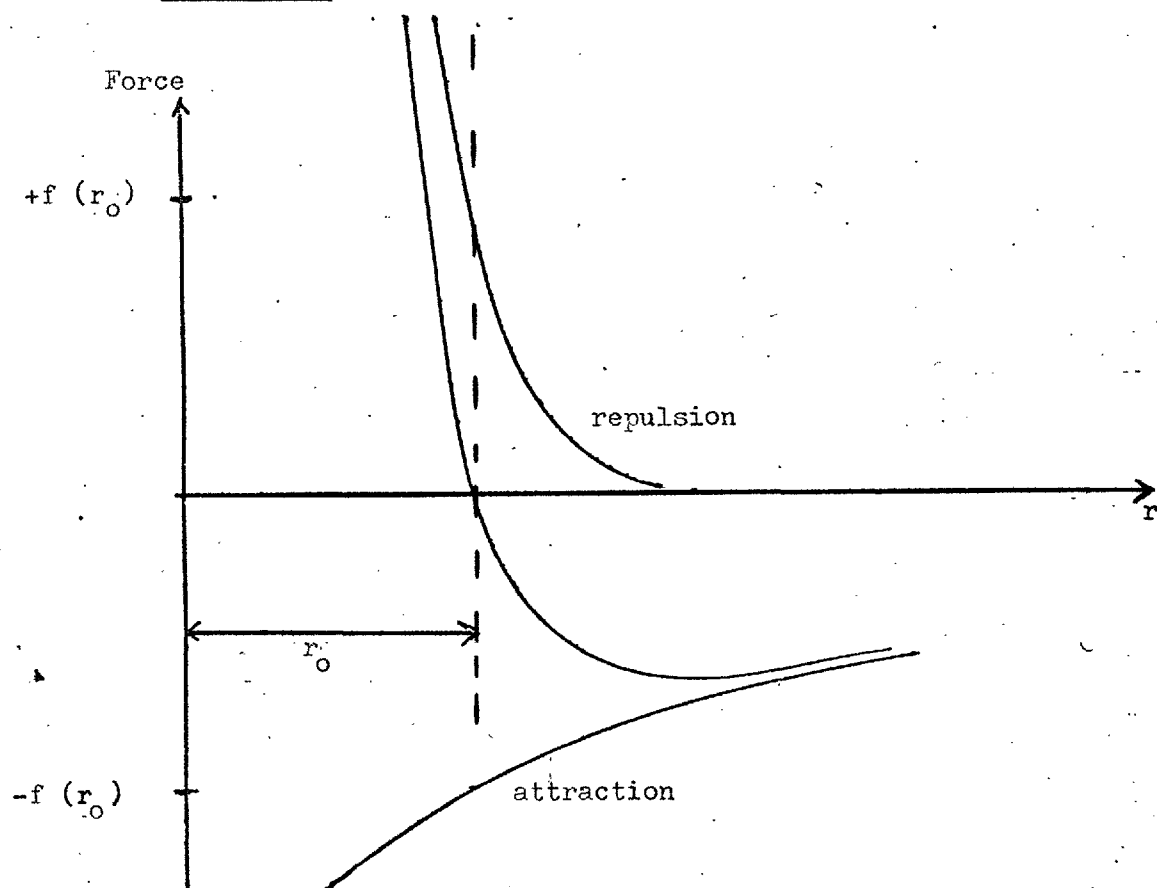


Fig 3 (2) Interaction force as a function of distance between two particles.

Three basic types can be distinguished.

(1) Orientational Interactions.

Keesom (1) was the first to give a classical treatment between permanent dipoles which results in a mutual orientation of the two dipoles corresponding to a minimum potential energy of the system.

(2) Induction Interaction.

Debye (2) introduced an induced temperature independent term to explain temperature dependence caused by displacements of centres of gravity of electric charges in particles under the effect of a Molecular Field.

But the Keesom-Debye Theory cannot explain the observed interaction between molecules that have no permanent electric dipoles i.e. the type that occur in systems of paraffin and fatty acid crystals.

(3) London (3) was the first to explain this phenomenon in terms of quantum mechanics - the London dispersion force appearing as second order perturbation terms.

In very simple terms the dispersion terms appears as follows, see figure 3 (3), using two hydrogen atoms as an example.

The molecule has no dipole moment, as the probability of finding the electron at any point on the circular orbit is the same, hence the average dipole moment is zero. However at any given instant the molecule does have an electric moment equal to er . Widely different relative spatial orientations are possible corresponding roughly to attractive and repulsive configurations as shown.

It can be shown from Quantum Mechanics that the system exhibits long range London forces when considering second order perturbations of preferred unsymmetrised wave function and short range repulsive forces when considering first order perturbations of the symmetrised wave function.

London's conclusion was that the energy of attractive interaction between an instantaneous dipole moment of a fluctuating dipole in one molecule and the dipole it induces in the other is inversely proportional to the sixth power of the distance between them.

$$\text{i.e. } U_D = -\frac{C}{r^6} \quad - (5)$$

Slater and Kirkwood (4) using a variational method obtain the more accurate formula

$$U_D = -\frac{3}{4} \frac{eh}{r^6} \left(\frac{N\kappa^3}{m} \right)^{\frac{1}{2}} \quad - (6)$$

Where e = charge of electron

m = mass of electron

N = number of electrons in atomic shell

α = polarizability of molecules.

Thus the total Van der Waals interaction energy of a neutral system is

$$U = U_0 + U_1 + U_D \quad - (7)$$

It can be shown that the dispersion forces contribute practically all the force to a system for small electric moments.

The most important property of dispersion forces is that they are additive within the limit of their range and do not display a saturation point. This means that in a neutral system such as a boundary layer the total force on a molecule is the sum of the individual forces between the molecule and its relevant neighbours.

The theory of dispersion forces breaks down completely at very short distances and requires correction at distance above 200 Å. The latter are termed retardation forces due to Casimir and Polder (5) and are attributed to the finite time electromagnetic wave take to travel a larger distance, the resulting potential takes the form of an inverse seventh power law. The theory of Intermolecular forces is covered in detail in reference (6)

3.3 Interactions between condensed phases

The problem occurs when extending the theory between particles and molecules to solids and condensed phases. Much work in these aspects has been done by Lifshitz (7), and for a theory of boundary friction the results for two parallel infinite planes may be quoted.

$$\text{i.e. } U = \frac{-A}{12\pi H^2} \quad - (8)$$

$$\text{and } U = \frac{-A}{30\pi H^3} \quad - (9)$$

H is the layer height

Where (8) applies to dispersion forces and (9) to retardation effects at longer range. A equals $\pi^2 q^2 C$, q being the volume density of the molecules and C being London's constant - Reference (8).

3.4 Repulsive forces.

In contrast to attractive forces relatively little is known about repulsive forces. The theoretical origins are clear enough but the detailed calculations and equations of interaction are usually in disagreement with each other. (9); (10); (11); (12); (13).

When two atoms are brought together their charge distributions gradually overlap (Figure 3 (4)), thereby changing the energy of the system by creating distortions in their distributions, which are required by the Pauli Exclusion Principle. This states that no two

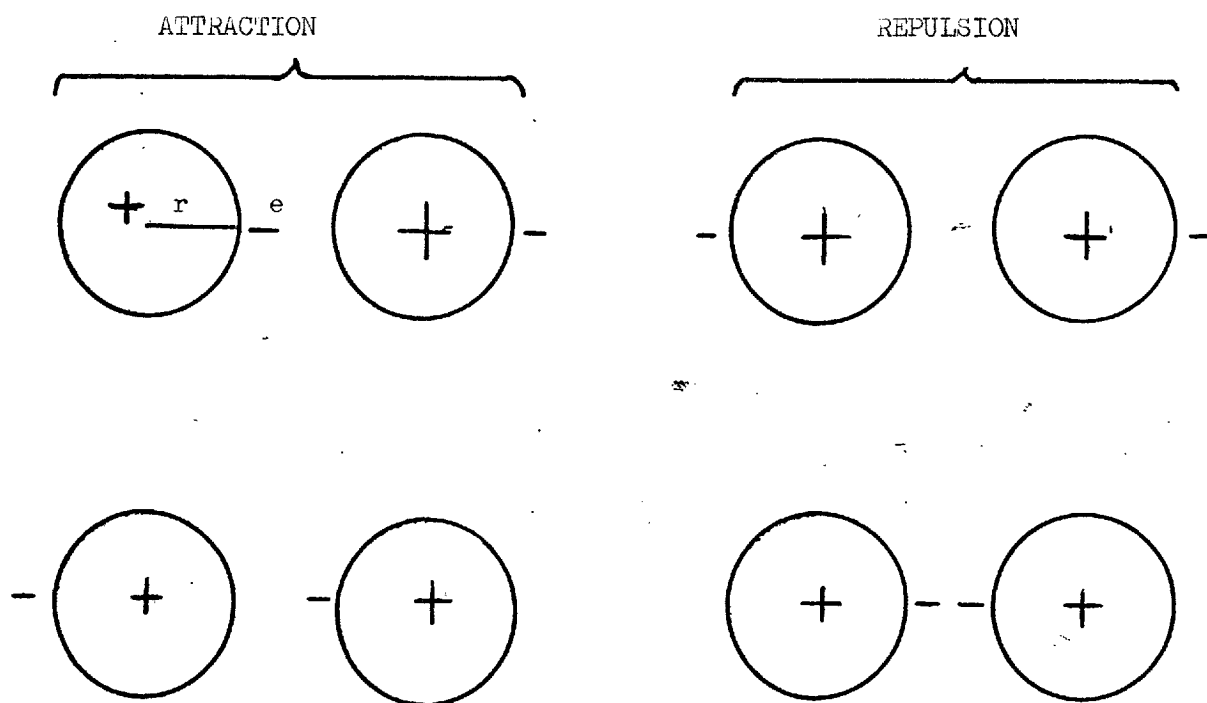


Fig. 3 (3) Representation of origin of attractive and repulsive potentials.

electrons can occupy the same quantum state, therefore some electrons must be promoted to unoccupied higher energy states. This increases the total energy of the system and gives an overall repulsive contribution to the interaction.

All repulsive potentials appear as first order perturbations with symmetrised wave functions obeying the Exclusion Principle. As shown by equation (4) repulsive potentials may be represented by a power law and equation (10) is termed the Lennard-Jones potential, the parameter B is determined by measurement to fit a particular system.

$$R_r = \frac{B}{r^{12}} \quad - (10)$$

The same sort of arguments are used to explain Co-valent

bonds e.g. to explain the extreme strength of hydrocarbon chains in paraffins and fatty acids. But in this case it is found that the most stable form is not affected by the Exclusion Principle and the electrons concerned may be imagined being shared by the atoms. The other state possible is a parallel situation to figure 3(4). See figure 3 (5).

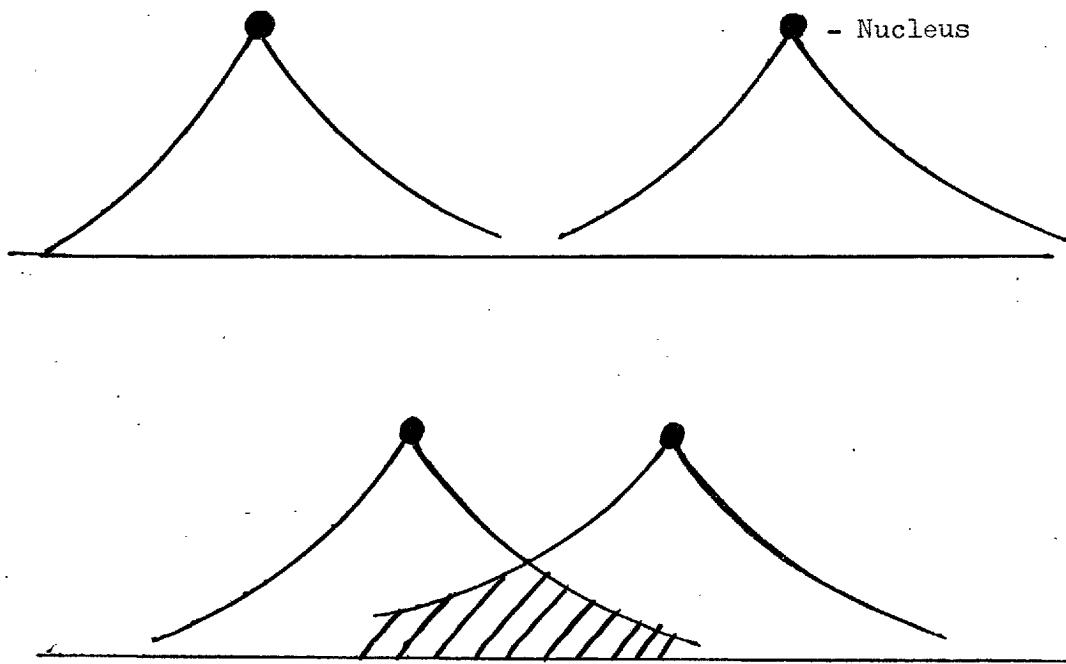


Fig. 3 (4) Electronic charge distributions overlapping as atoms approach each other.

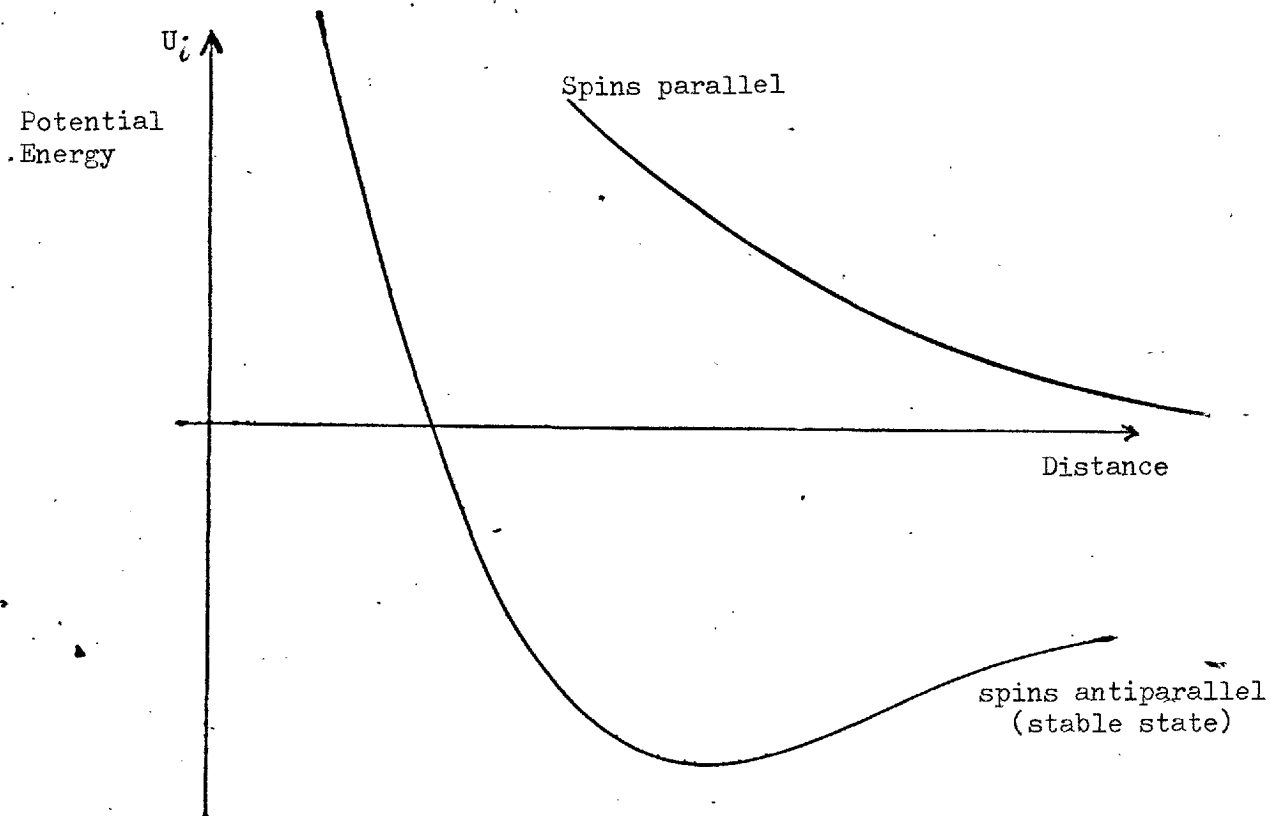


Fig. 3 (5) Explanation of stability of Co-valent Bond

3.5 Summation of Forces

As stated by Margeneu (12) it seems rather a dubious procedure to sum the attractive and repulsive forces at intermediate distances as they are derived by inconsistent approximations. However since a good theoretical method is lacking most authors use a modified

'Buckingham' or '6 - exp' potential of the form (14)

$$U(R) = -AR^{-6} + B \exp(-CR) \quad - (11)$$

Where the repulsive term is an exponential function with two coefficients B and C, these can be used to vary the hardness of the potential to suit different properties of the model.

3.6 Suitability to model

The total interaction potential is taken as the sum of the attractive and repulsive components at all distances even though at short range (1Å) the dispersion forces are no longer valid. These short distances were never encountered, but even so the repulsive forces would be huge in comparison. Long chain even hydro-carbons can be shown to be electrically neutral in a stress free system and odd chains shown to have an extremely small resultant moment equal to one methylene contribution. The methyl end group is always neutral. (16)

From these considerations any attractive force contribution was taken to be the total sum of dispersion forces between the configurations of neutral carbon and hydrogen atoms. As polarizability is also additive the Slater-Kirkwood formula (equation 6) can be adapted to give coefficient for C-C, C-H, H-H, and CH₂ groupings i.e. treating methyl and methylene groups as scattering centres or as interaction centres coinciding with the nuclei of the C and H atoms.

The repulsive forces are the most important for a boundary lubricating system or any system of crystal formation. Whittington and Chapman (16) in connection with a Monte Carlo study of Rotational Premelting in Crystals of paraffins showed the anisotropy of internal energy is due largely to repulsion energy, the dispersion energy acting as a constant background holding the molecules together. Similarly Broadhurst (17) found "the repulsion energy had the same general angular dependence as the total energy," It is also stated that C-C and C-H repulsion will play a considerably less important part than H-H repulsion and to a first approximation can be neglected.

Salem (18) also showed that the extremely localised repulsive forces are additive as long as no two overlap densities occupy the same region of space. Due to the nature of the model and nature of

the repulsive functions it was found in any case that the total repulsive force being the sum of equal contributions was rare.

3.7 Combinations of potentials

The Slater-Kirkwood attractive energy formula was used to derive the coefficients 22.6 and 8.68 in kcal/mole $\times \text{\AA}^6$ for CC and CH contributions respectively and 595.0 kcal/mole for Scattering Centre results.

In combination with the above attractive potentials five different '6 - exp' H-H potential are used, varying from soft through to hard

(a) Barton (19)

$$U(R) = -3.397 R^{-6} + 13.207 \exp(-2.434 R) \quad - (12)$$

(b) Hendrickson (20)

$$U(R) = -3.573 R^{-6} + 15.93 \exp(-2.434 R) \quad - (13)$$

(c) Hendrickson - Bartell (21)

$$U(R) = -3.573 R^{-6} + 21.66 \exp(-2.497 R) \quad - (14)$$

(d) Bartell (22)

$$U(R) = -3.573 R^{-6} + 10.51 \exp(-2.160 R) \quad - (15)$$

(e) Muller (23)

$$U(R) = -4.496 R^{-6} + 100.9 \exp(-2.645 R) \quad - (16)$$

(f) Slater (24)

$$U(R) = -3.573 R^{-6} + 770.0 \exp(2.43 R) \times 10^{-12} \quad - (17)$$

All the attractive potential are based on Slater-Kirkwood. The coefficients are expressed in atomic units except Slater's repulsion term, which is in ergs. The larger the coefficient B (equation 11) or the small C the harder the resulting potential will be.

In addition one Lennard-Jones potential was used with coefficient 1.35×10^4 kcal/mole. Hirschfelder (9) has used an empirical curve fitting method to produce.

$$U(R) = AR^{-6} + 0.818 R^{5/2} \exp(-2R) \quad - (18)$$

As will be shown later, harder potentials were used in connection with compressability data by fitting polynomials to steeper H-H curves. All the above repulsive potentials were used with both the scattering centre and point charge attraction terms.

3.8 Program of H-H interaction curve

A program was written to plot the H-H interaction curves for equations (12); (13); (14); (15); (17) and (18) using an I.B.M. 1794 machine, utilizing a Calcomp Plotting Subroutine. The distances are in angstroms and the potentials in kcal/mole. See figures 3(6), 3(7), 3(8), 3(9), 3(10), 3(11), and 3(12).

```

C      PROGRAM TO PLOT HYDROGEN REPULSIONS POTENTIALS.
      DIMENSION RI(32),EB(32),EBA(32),EHSC(32),NUM(1)
      READ (5,1000) BUCK1,BUCK2,BUCK3,B1,B2,B3,BUK1,BUK2,BUK3,BUK4,BMUL,
      BSL,BLH,BH,CH,CSL,CMUL,BTLL,BEB,EART,CCN,ERG,AC,C3
      1000 FORMAT (10X,F11.5)
C      CONSTRUCT DE TUCP AND STEPS IN R
      DO 7-I=1,30
      IF (I.EQ.1) GO TO 18
      GO TO 19
18  RI(I)=1.0
      GO TO 20
19  RI(I)=RI(I-1)+0.1
20  CONTINUE
C      CALCULATE POTENTIALS.
      EB(I)=- (BUCK1*CCN*(AC**6))/(RI(I)**6)+BUK1*EXP(-EART*RI(I)/AC)*CON
      EBA(I)=- (BUCK2*CCN*(AC**6))/(RI(I)**6)+BUK4*EXP(-BTLL*RI(I)/AC)*CON
      EHSC(I)=- (B1*(AC**6))/(RI(I)**6)+B2*(AC**8)/(RI(I)**8)+B3*(AC**10)/(RI(I)**10)
      + (BH*(RI(I)**(5/2)))*EXP(-CH*RI(I)/AC)/(AC** (5/2))*CON
7  CONTINUE
C      PLOT GRAPHS.
      NUM(1)=30
      CALL START
      CALL SYMBCL(12.0,10.0,0.25,7H=EARTCN,0.0,7)
      CALL GRAP (R,EB,NUM,1,+2,25.0,13.0)
      CONTINUE
      CALL PLOT (27.0,0.0,-3)
      CALL SYMBCL(12.0,10.0,0.25,8H=EARTCL,0.0,8)
      CALL GRAP (R,EBA,NUM,1,+2,25.0,13.0)
      CONTINUE
      CALL PLOT (27.0,0.0,-3)
      CALL SYMBCL (4.0,1.0,0.25,13H=HIRCSFELDER,0.0,13)
      CALL GRAP(R,EHSC,NUM,1,+2)
      CALL ENPLOT (0.0)
      CONTINUE
      STOP
      END

```

Fig. 3 (6) - Program for Hydrogen Interaction Potential

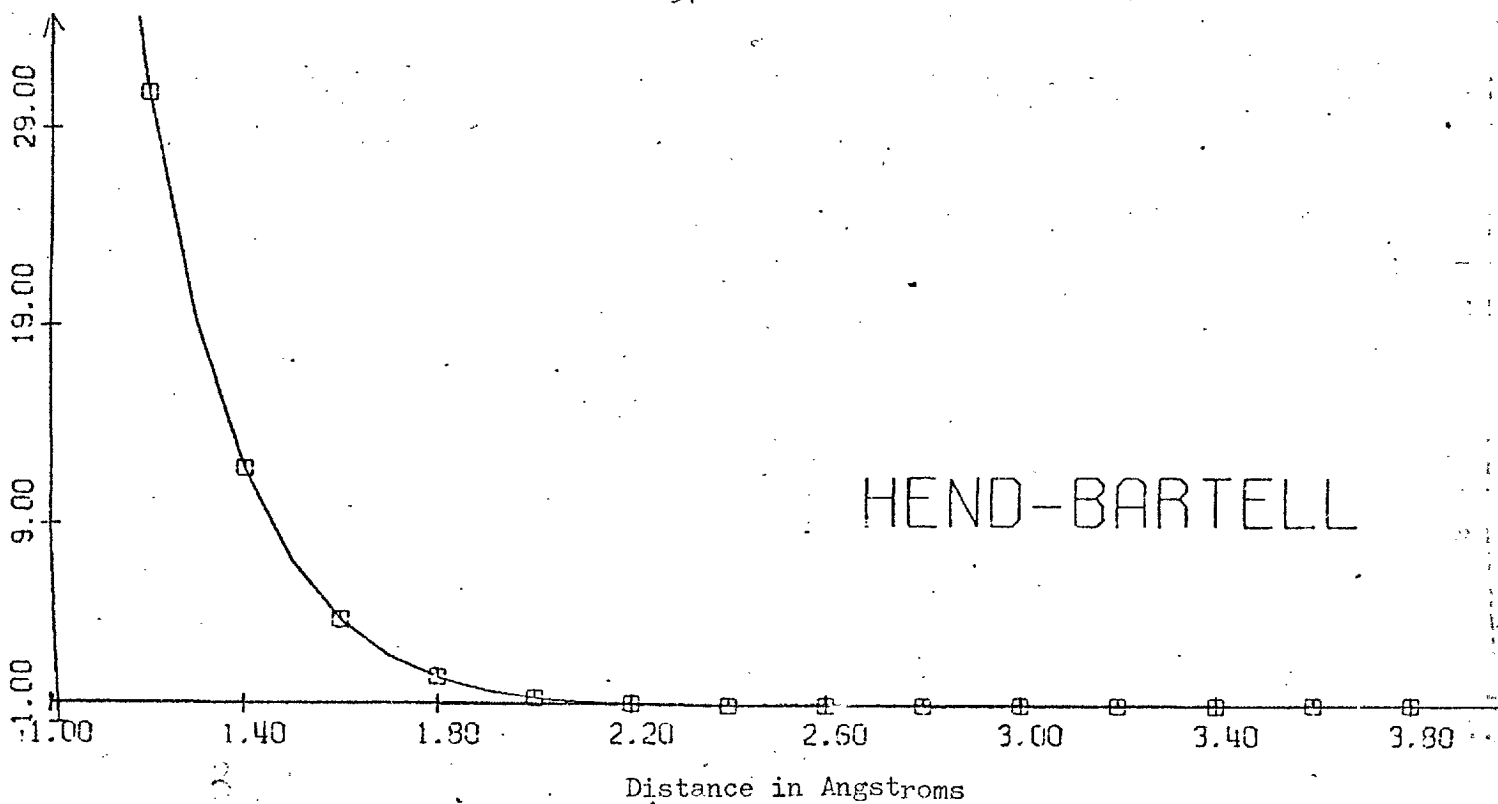


Fig 3 (7) Graph H-H interaction curve - see equation (14)

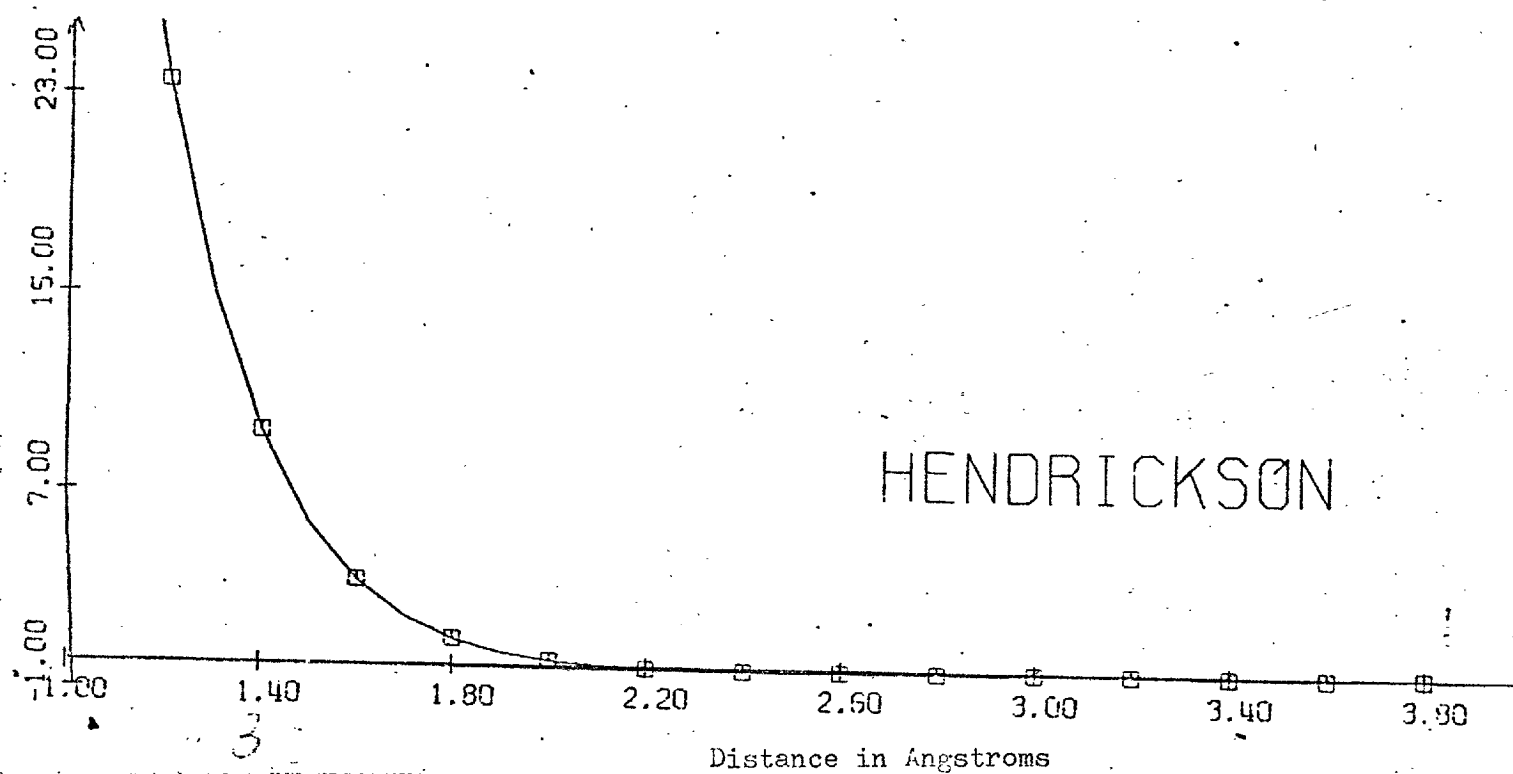


Fig 3 (8) Graph of H-H interaction curve - see equation (13)

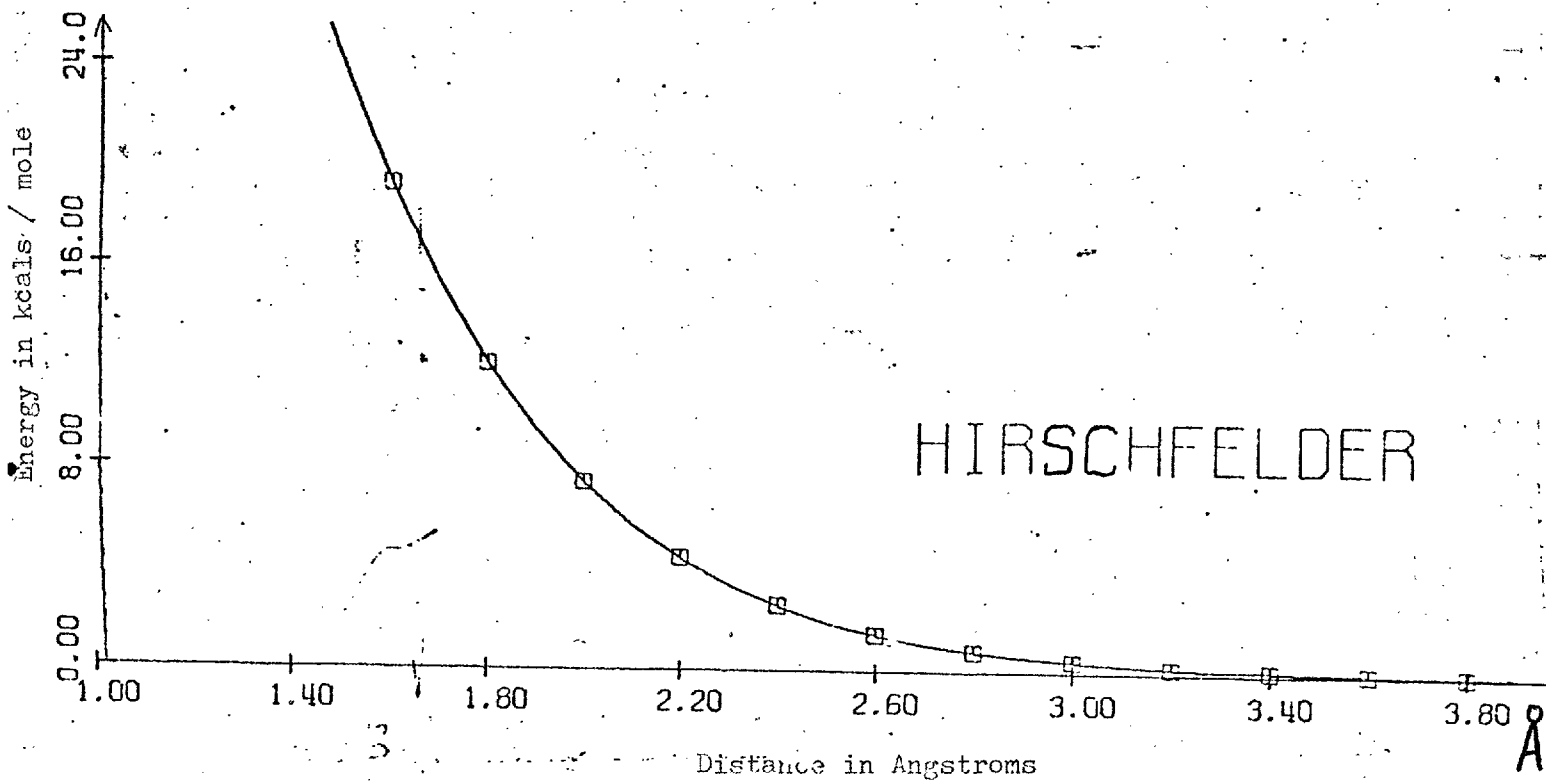


Fig 3 (9) Graph of H-H interaction curve - see equation (18)

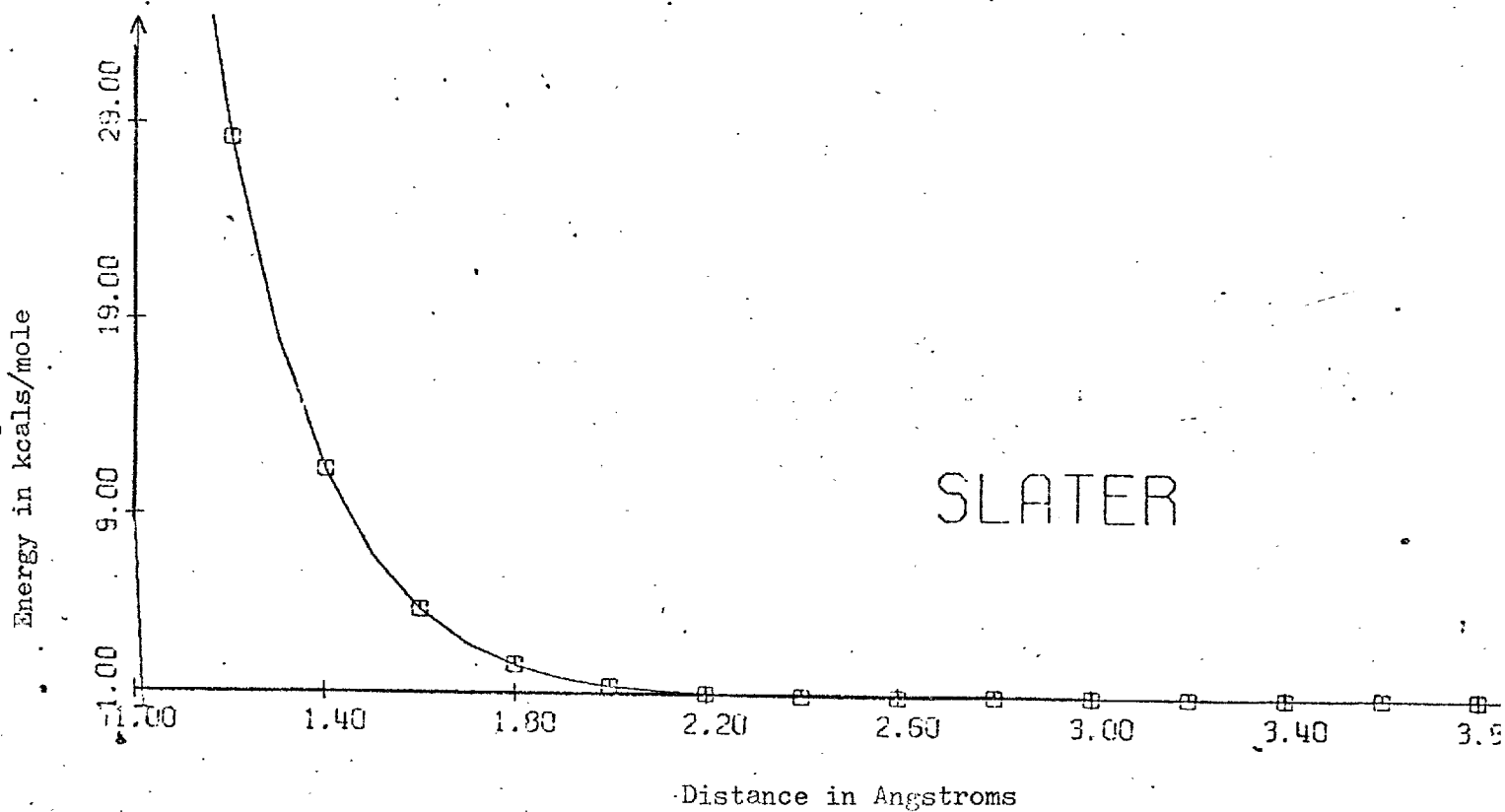


Fig 3(10) Graph of H-H interaction curve - see equation - (17)

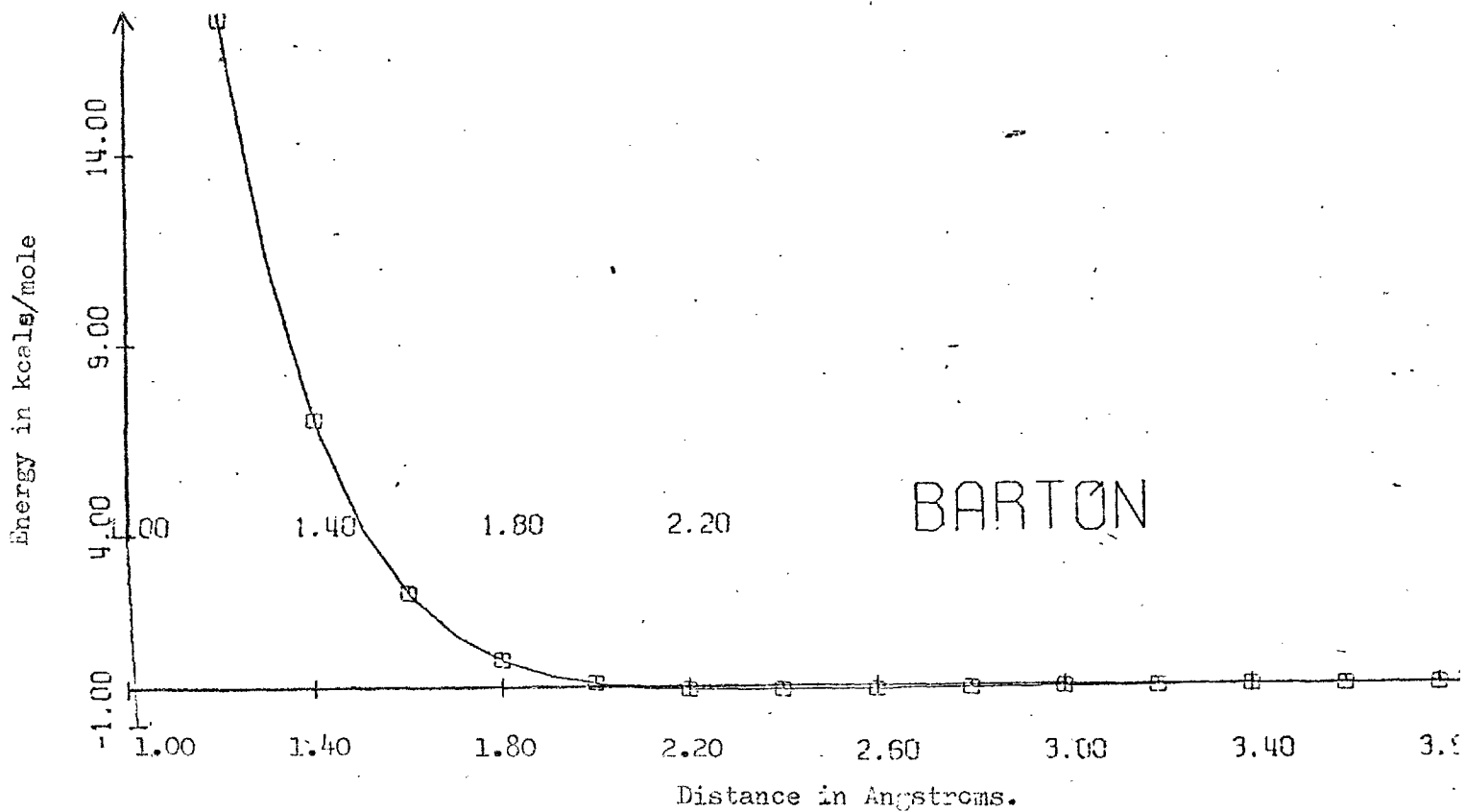


Fig. 3 (11) Graph of H-H interaction curve - see equation (12)

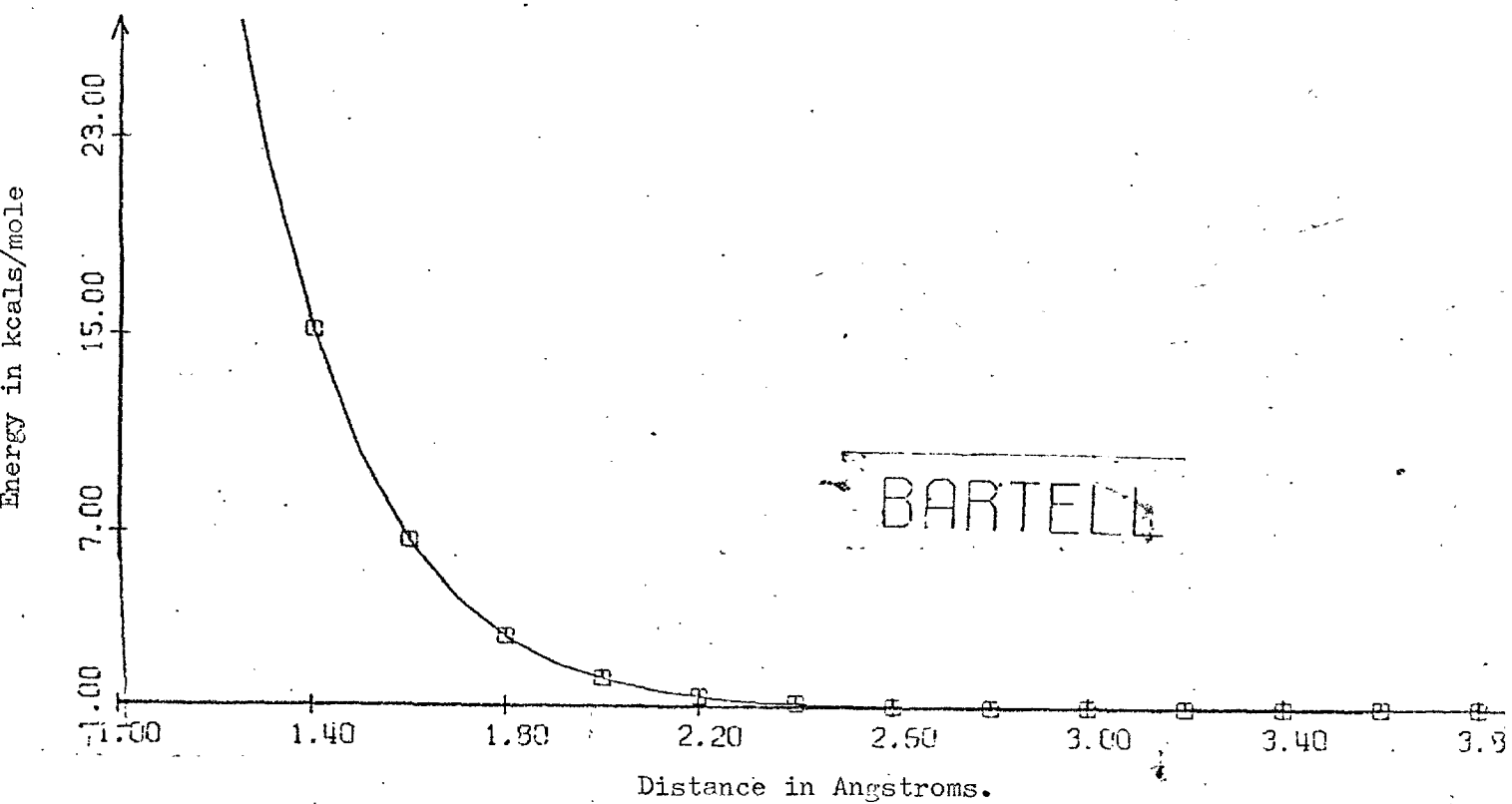


Fig. 3 (12) Graph of H-H interaction curve - see equation (15)

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CHAPTER 4 - FUNCTION AND PARAMETERS OF MAIN PROGRAMS

4.1 Introduction

The model is considered to be a molecular lattice of paraffin - which can be adapted to suit fatty acids. In particular the same structure of paraffin crystals as used by Cameron was constructed. The exact angles and dimensions as stated by the evidence of X-ray and electron diffraction methods, were used in computer programs to obtain models of fatty acids in boundary lubrications. These programs could be used to shear layers, compress them, tilt and rotate radicals and shift the orientation to the vertical. How these programs were written and tested will be described in this chapter and the following one.

4.2 LATTICE and CHAIN Dimensions

The structure of the paraffin $C_{29}H_{60}$ in its orthorhombic structure as studied by Müller (1) is shown in figure 4 (1) and the basic atomic structure of methylene chains is shown in figure 4(2).

In figure 4(1), $RX = 7.426 \text{ \AA}$, $RY = 4.956 \text{ \AA}$, $CK = 0.94 \text{ \AA}$, and $CM = 2.773 \text{ \AA}$ which are the basic lattice reproduction parameters in the X and Y Direction. The angle (γ) of inclination of the chains to the X-axis in the XY plane is termed the Setting Angle and is the minimum energy or equilibrium position of the molecules. The end methyl group is shown in black - the spacial arrangement of the H atoms is not shown.

In figure 4(2) the basic tetrahedral structure of methylene chains is shown. In the Z plane the tetrahedral angle 2θ is between the C-C bonds, and is equal to $109^\circ 28'$. Two hydrogen atoms are linked to every carbon atom also by the tetrahedral angle. The repeat distance of the chain ($2.54 \text{ \AA}$) is as shown, similarly the CH distance is $1.096 \text{ \AA}$.

The theory is primarily concerned with the effect of shear of one layer over the next along the methyl slip plane. Thus referring to figure 4(1) an arbitrary co-ordinate system is constructed to coincide with a 'top molecule' as shown, with the Z axis vertically out of the diagram.

To calculate distances between any two molecules (CC,CH,HH) all bonds distances are resolved into XY and Z components using known parameters. i.e. in the XY plane the C atoms have components X and Y relative to the origin. Using fig. 4 (2),

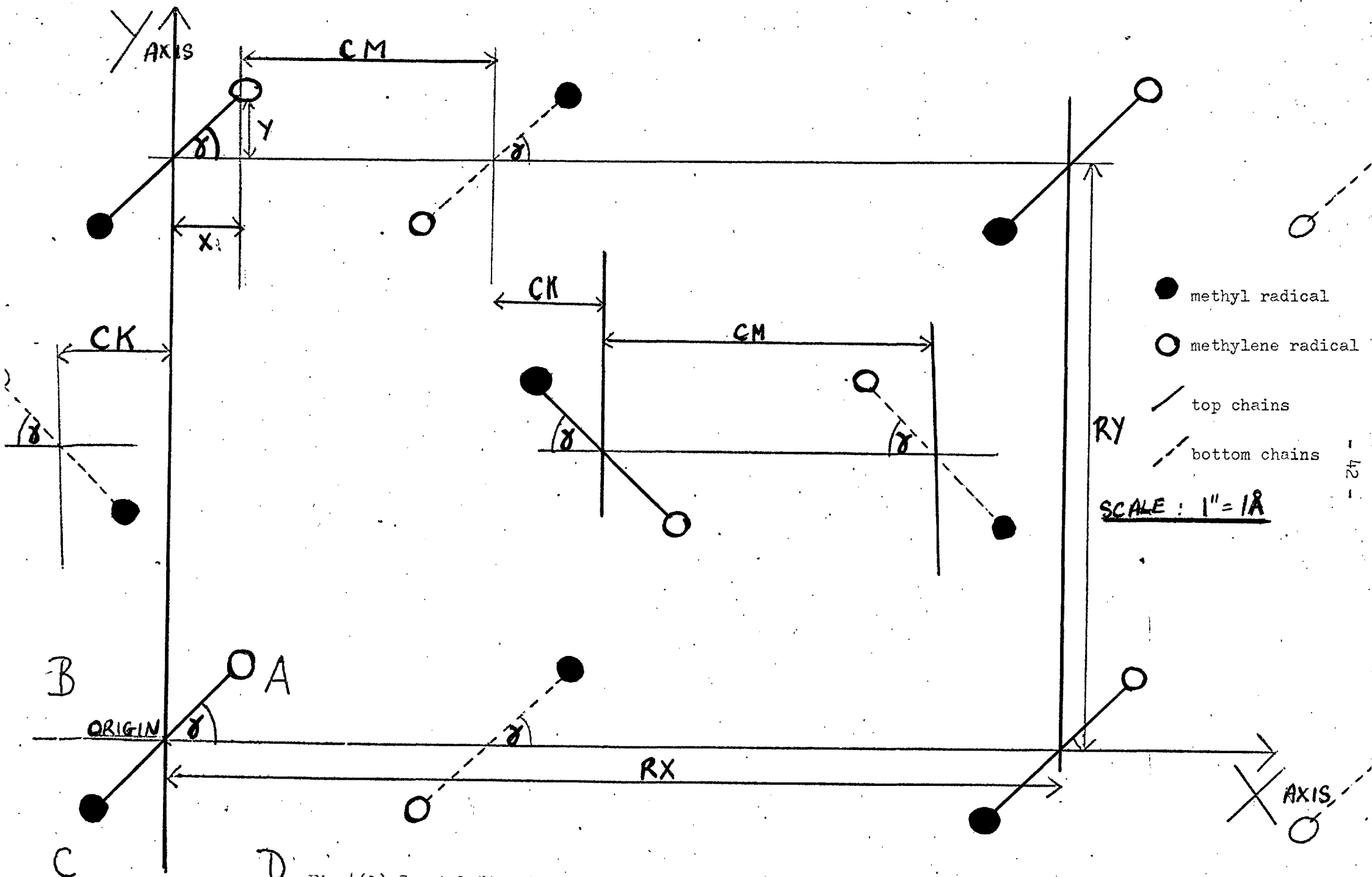
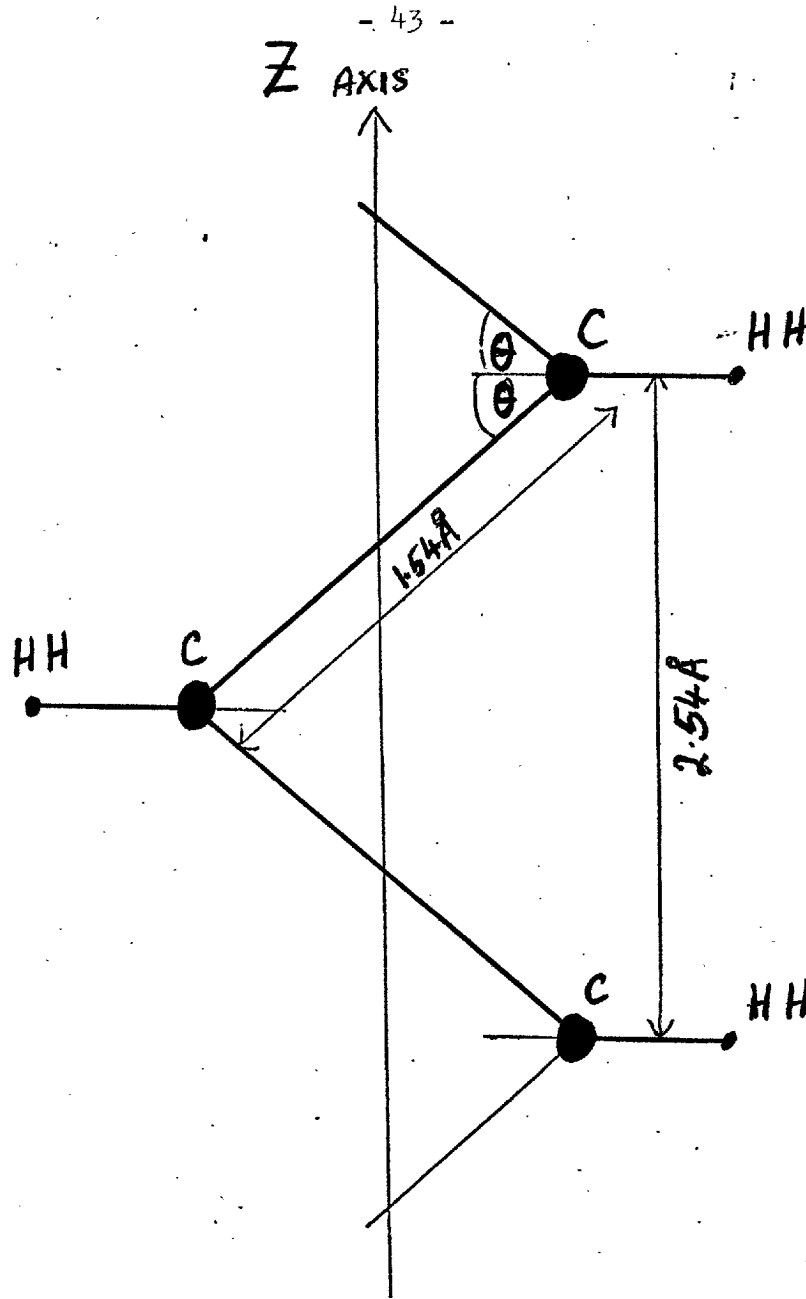


Fig 4(1) Crystal Structure of monoparaffin $C_{29}H_{60}$ in XY plane

(a) Z PLANE



(b) XY PLANE

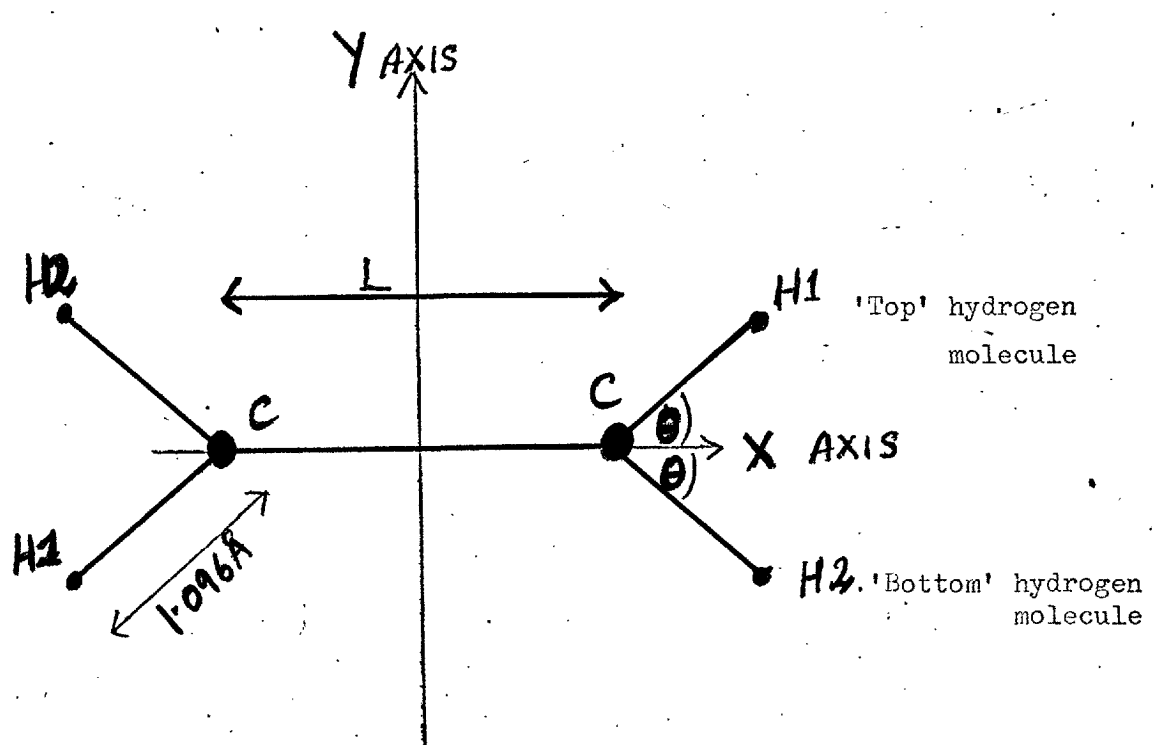


Fig. 4(2)

Atomic structure of methylene chain.

$$L = 1.54 \cos \theta$$

Therefore

$$X = \frac{L}{2} \cos \gamma \quad - (1)$$

$$Y = \frac{L}{2} \sin \gamma \quad - (2)$$

By using the properties of the function sin and cosine the following Boundary Conditions apply

- (i) $\gamma = 0$ $X = L$, $Y = 0$
- (ii) $\gamma = 90^\circ$ $X = 0$, $Y = L$
- (iii) $\gamma = 180^\circ$ $X = -L$, $Y = 0$
- (iv) $\gamma = 270^\circ$ $X = 0$, $Y = -L$

4.3 The Summation Arrays

By using figure 4(1) as the basic building unit then reproducing it the whole lattice can be derived. The diagram can represent two concepts (1) Summing of attractive potentials by scattering centres in which case the $\text{CH}_2 - \text{CH}_2$ distances are smaller than the exact atomic dimensions given in figure 4(2), (2) the first stage in summing of point interaction sites i.e. just C-C distances.

From figure 4(1) it can be seen that four classes of distances can be distinguished (i) CH_3 and CH_2 groups of top molecule with CH_2 groups of bottom molecule. ($\bullet$ (T) - $\bullet$ (B)) - (3) similarly,

$$(ii) \bullet (T) - \bullet (B) \quad - (4)$$

$$(iii) O (T) - \bullet (B) \quad - (5)$$

$$(iv) O (T) - O (B) \quad - (6)$$

Obviously some of these classes of distances when taken quadrant by quadrant (A,B,C,D in fig. 4(1)) will be the same because they are all derived using the parameters R_X, R_Y, X, Y, CM, CK .

The following convention for the summation is introduced when writing the programs. The first letter of each summation array refers to the Quadrant (A,B,C,D), the second to the two orientations (A, B - see fig 4 (1)) and the third to the XY orientation.

i.e. Considering; $\bullet$ (T) - $\bullet$ (B) the following arrays are possible.

The indices I and J signify the reproducibility of the lattice, taking the value I = 1, 7 and J = 1, 10 i.e. $R_X (1) = 0.0$; $R_X (2) = 7.426$, $R_X (3) \dots \dots \dots R_X (7) = 44.556$ and $R_Y (1) = 0.0$, $R_Y (2) = 4.956 \dots \dots R_Y (10) = 44.704$

$$\text{Therefore } AAX (I) = CM + 2X + R_X (I)$$

$$ABX (I) = R_X - CK + 2X + R_X (I)$$

```

AAY (J) = 2Y + RY (J)
ABY (J) = RY/2 + RY (J)
BAX (I) = RX - CM - 2X + RX (I)
BBX (I) = CK - 2X + RX (I)
BAY (J) = AAY (J)
BBY (J) = ABY (J)
CAX (I) = BAX (I)
CBX (J) = RY - 2Y + RY (J)
CBY (J) = RY/2 + RY(J)
DAX (I) = AAX (I)
DBX (I) = ABX (J)
DAY (J) = CAY (J)
DBY (J) = CBY (J)

```

This specific orientation must be used with one Z array to give a complete sum of distances - (see fig. 4(3)) - as the above arrays can only be used in certain combinations to give any meaning at all.

Thus the fundamental summing procedure using the applicable array RZ01 (M) as following bearing in mind that the sum of inverse sixths is required.

```

S1 = 0.0
D01 I = 1, 7, 1
D01 J = 1, 10, 1
D01 M = 1, 6, 1
S1 = S1 + 1.0/ [(AAX (I)2 + AAY (J)2 + RZ01 (M)2 ) **3] + 1.0/ etc.
1 CONTINUE

```

This utilizes a nested do-loop technique and is in effect the summing up of a three dimensional matrix.

The same method is used for the class ● (T) - O(B) yielding the following arrays

```

i.e. AAXE (I) = CM + RX(I)
ABXE (I) = RX - CK + RX(I)
AAYE (J) = RY(J)
ABYE (J) = RY/2.0 + 2Y + RY(J)
BAXE (I) = RX - CM + RX(I)
BBXE (I) = CK - RX(I)
CAYE (J) = RY (J)
CBYE (J) = RY/2.0 - 2Y + RY(J)

```

As will be shown later when parameters describing displacement are described two of the above arrays are changed to

```

AAYE(J) = AY(J) = RY(J) ± D*SIN (F (MF) )

```

Fig 4 (3) Summation Chart for orientation ● (T) - ● (B) in XY plane, used in CC subroutine

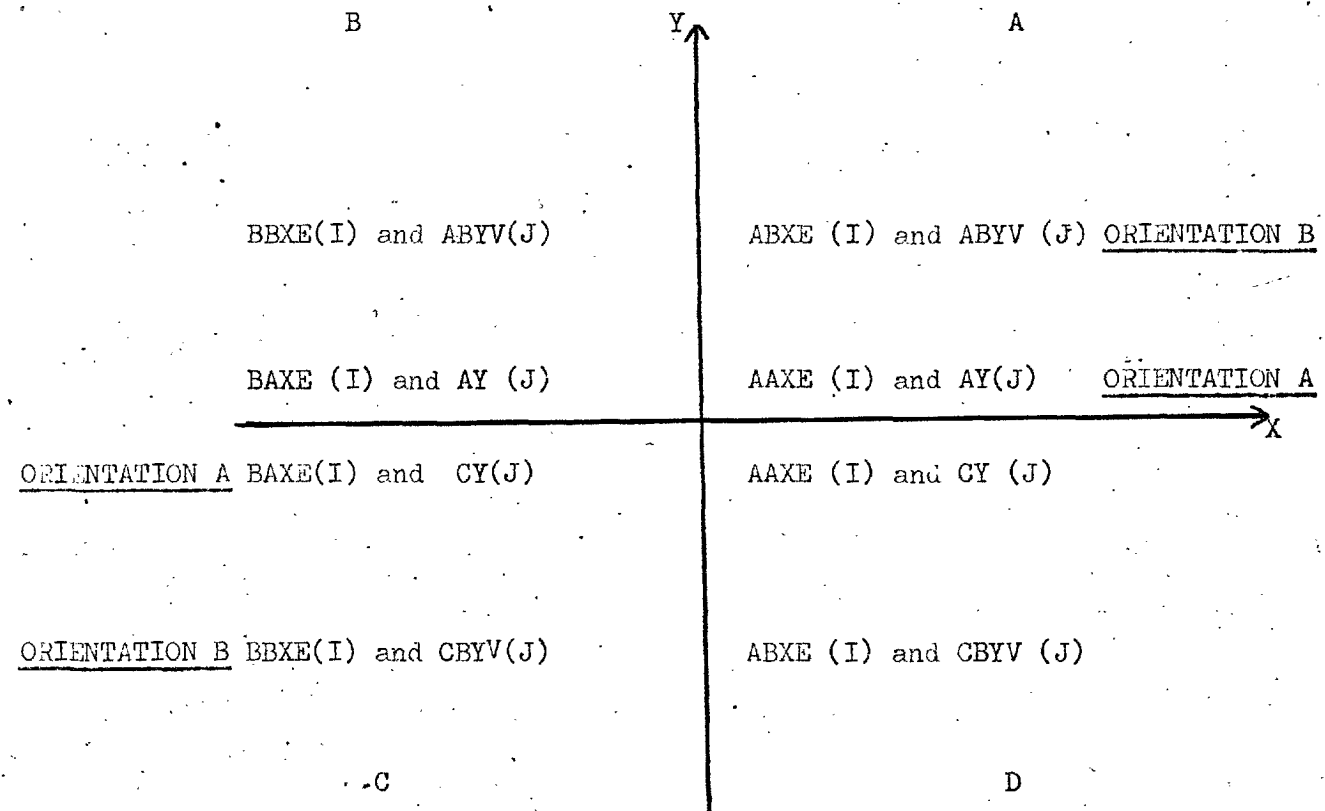
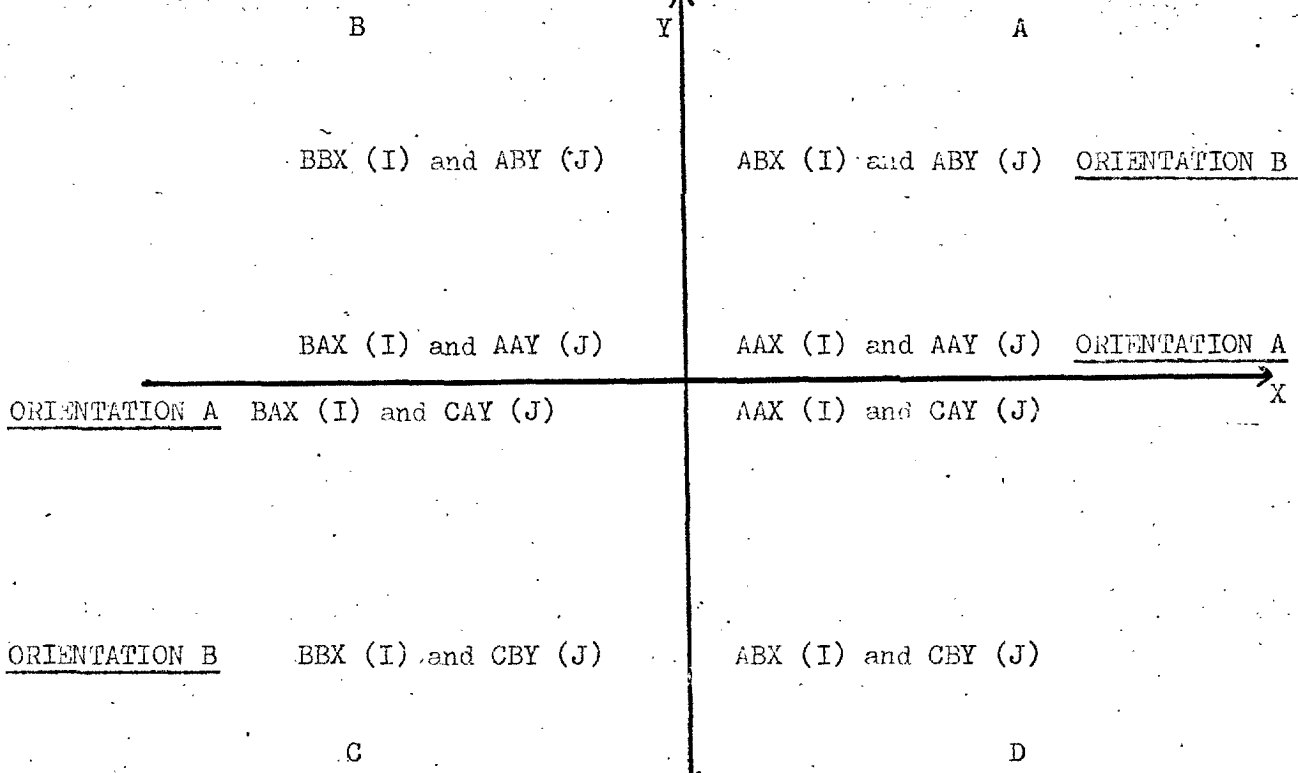


Fig. 4(4) Summation Chart for orientation O (T) - ● (B) in XY plane, used in CC subroutine

$$CAYE(I) = CY(J) = RY(J) + D * SIN[F(MF)]$$

These XY arrays are then combined with the Z array RZE1 (L) in a similar pattern to fig 4(3).

It can be seen from fig. 4(5) when dealing with the four expressions (3), (4), (5) and (6) due to the symmetry properties of the parallelogram (WXYZ), that expressions (3) and (5) could be equal. In fact this is the case except for the Y co-ordinates of orientation B - causing the new arrays below to be introduced.

$$ABYV(J) = CY/2.0 - 2Y + RY(J)$$

$$CBYV(J) = CY/2.0 + 2Y + RY(J)$$

This leads to the combination of XY arrays for orientation [O(T) - ●(B)] with Z array RZE1 (P), see fig. 4(4).

The only remaining orientation is expression (6), from fig. 4(5) this is the other diagonal of the parallelogram, in conjunction with fig. 4(1) gives the new arrays.

$$AAXD(I) = CM - 2X + RX(I)$$

$$ABXD(I) = RX - CK - 2X + RX(I)$$

$$AAYD(J) = RY(J) - 2Y$$

$$BAXD(I) = RX - CM + 2X + RX(I)$$

$$BBXE(I) = CK + 2X + RX(I)$$

$$CAYD(J) = RY + 2Y + RY(J)$$

$$ABYD(J) = ABY(J)$$

$$CBYD(J) = CBY(J)$$

These XY arrays are combined similarly to fig. 4(3) together with the array RZD1 (Q).

4.4 Z arrays, screening effects and weighting factors.

By considering fig. 4(5) three Z arrays can be formed

$$RZE1(L) \quad , \quad 1' - \textcircled{1} \text{ and } 1 - \textcircled{1}'$$

$$RZO1(M) \quad , \quad 1 - \textcircled{1}$$

$$RZD1(Q) \quad , \quad 1' - \textcircled{1}'$$

These correspond to expressions (3), (4), (5), (6) as shown. The model assumes the Van der Waal forces are additive and that there is no screening of the forces. This means that contributions to the attractive forces take place from the source molecules at point 4 (fig. 4(5)) with point $\textcircled{1}$ as well as point 1 with point $\textcircled{4}$.

By considering the diagram there is evident symmetry in the Z direction and to accommodate all the interactions possible while saving computing time, one set of interactions can be weighted.

$$\begin{array}{ll} \text{i.e. } 1 - \textcircled{1} & \text{times one} \\ 1 - \textcircled{2} & \text{times two} \\ 1 - \textcircled{3} & \text{times three} \quad \text{etc.} \end{array}$$

to whatever range is required.

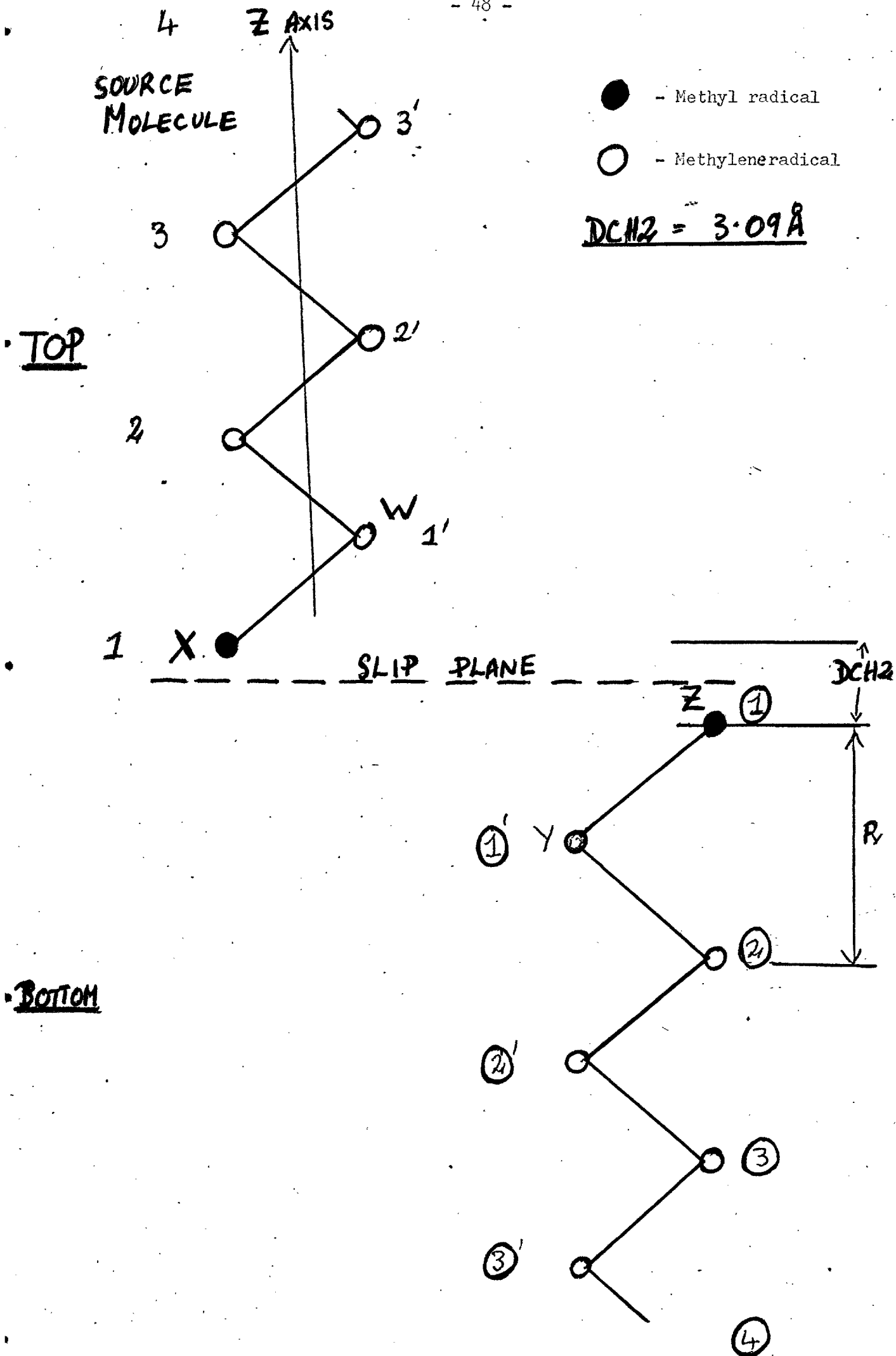


Fig. 4(5) Diagrammatic form of Z - Axis showing weighting factors.

4.5 Co-ordinates of Hydrogen atoms in methylene groups

Fig. 4(6) depicts a plan view of a hydrocarbon chain in the orientation A position. The angle γ is the Setting Angle and θ the tetrahedral angle, the two hydrogen atoms will have different absolute co-ordinates X_1, X_2, Y_1, Y_2 relative to an origin located at the Carbon atom C.

As before with the Carbon co-ordinates X, Y the hydrogen atoms can be resolved in X and Y directions. Consider the CH bond length as HC

$$\text{therefore } X_1 = HC \cos (\theta - \gamma) \quad - (7)$$

$$Y_1 = HC \sin (\theta - \gamma) \quad - (8)$$

$$X_2 = HC \cos (\theta + \gamma) \quad - (9)$$

$$Y_2 = HC \sin (\theta + \gamma) \quad - (10)$$

The mirror orientation B can be treated exactly the same way to give equations (7) to (10)

4.6 Co-ordinates of Hydrogen atoms in methyl groups.

Fig. 4(7) shows a three dimensional view of a methyl end group. Again the co-ordinates (X_3, Y_3, Z_3) refer to the origin C and give absolute distances relative to C.

By considering triangles (H_1, H_2, C) , (A, C, H_3) and using the Cosine Rule, angle α equals $34^\circ 46'$, hence it follows

$$X_3 = HC \sin \alpha \cos \gamma \quad - (11)$$

$$Y_3 = HC \sin \alpha \sin \gamma \quad - (12)$$

$$Z_3 = HC \cos \alpha \quad - (13)$$

By calculating Z_3 ($0.9003\text{\AA}$) and using the known value of DCH₂ (see fig. 3(5)) the value of the Z component of the H₃ - H₃ distance, CRIT, at equilibrium can be found.

$$\text{i.e. CRIT} = (3.09 - 2 \times 0.9003) = 1.2894 \text{\AA}$$

This compares with Cameron's value of $1.29 \text{\AA}$.

4.7 CH and HH attractive potentials

By considering the spacial orientations of the hydrogen atoms (figs. 4 (6) and 4 (7) and equations (7) - (13)) in conjunction with fig. 4 (1) and by adding or subtracting combinations of the co-ordinates $X_1, X_2, X_3, Y_1, Y_2, Y_3$, to the summation arrays already discussed (section 4.3) any distance of any atom may be computed with respect to the source molecule. [3 new Z arrays were introduced to deal with the H₃ combinations].

The computed CH and HH distances were then summed as inverse sixth distances and used to obtain attractive Van der Waals potentials - these were used with the CC contribution to obtain the total attractive potential of atomic centres. See figs. 4 (8) and 4 (9).

4.8 HH Repulsive distances

For the purposes of the model only HH repulsive contributions are considered. As these are short range forces only nearest neighbour interactions need be considered with respect to the considered molecule. But as one unit cell is sheared over the adjacent layer, this will cause the nearest distances to be due to different pairs of hydrogen atoms. Thus in the program a range of 2-3 unit cells is considered, all the H-H distances of the methyl groups are computed and only distances less than $2.6 \text{ \AA}$ are considered. The repulsive subroutine uses part of the HH attractive subroutines array, but only using the nearest Z array values. The distances were computed and used in the repulsive formulae, with the inequality condition imposed to reduce unnecessary computing. See fig. 4 (12).

4.9 Displacement Parameters

Displacement is achieved by fixing the origin and shifting the reference molecule a distance D at an angle F (MF) with respect to the origin. Thus by adding or subtracting the X or Y component of the displacement to the appropriate summation arrays a new distance between the molecules can be formulated.

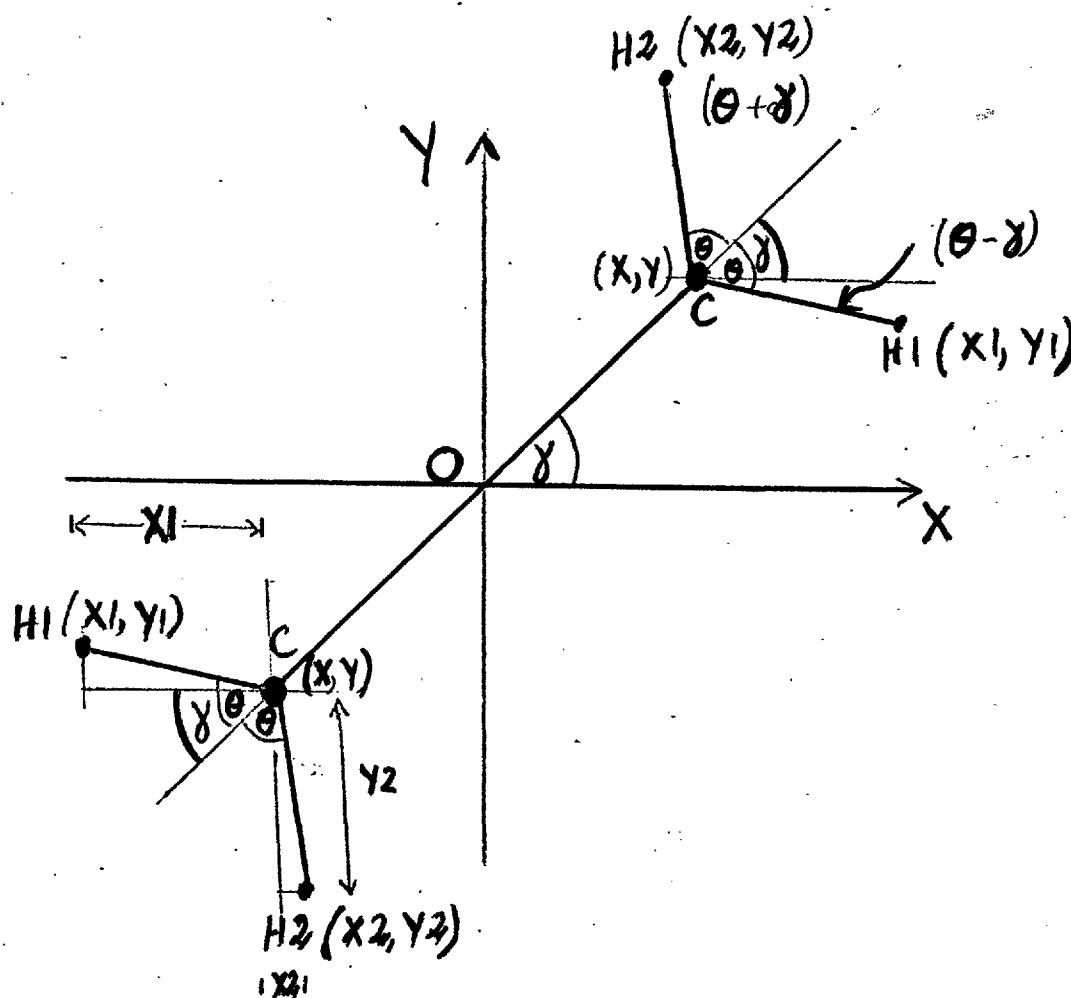


Fig 4 (6) Spatial orientation of methylene group.

An obvious Boundary Condition of the system is periodicity. Therefore the arrays have to be sufficiently large to impose the same cut off distance i.e. $25 \text{ \AA}$, at both ends of any periodic displacement.

(continued on page 57)

4.10 Setting Angle

The Setting Angle is implicit in the equations of X , Y , $X1$, $X2$, $X3$, $Y1$, $Y2$, $Y3$. Again an obvious Boundary Condition is a continuous potential relief when revolving the molecules about their Z axis.

4.11 Compression

A very important feature of the model is the effect of compression by a load. Compression can be achieved by using a simple Do-Loop to vary the parameter $DCH2$, the distance between the terminal methyl groups. This will in turn cause the H-H distances to decrease causing repulsion, similarly tension can be simulated by increasing the parameters $DCH2$. By using this technique with displacement, compression can be achieved anywhere.

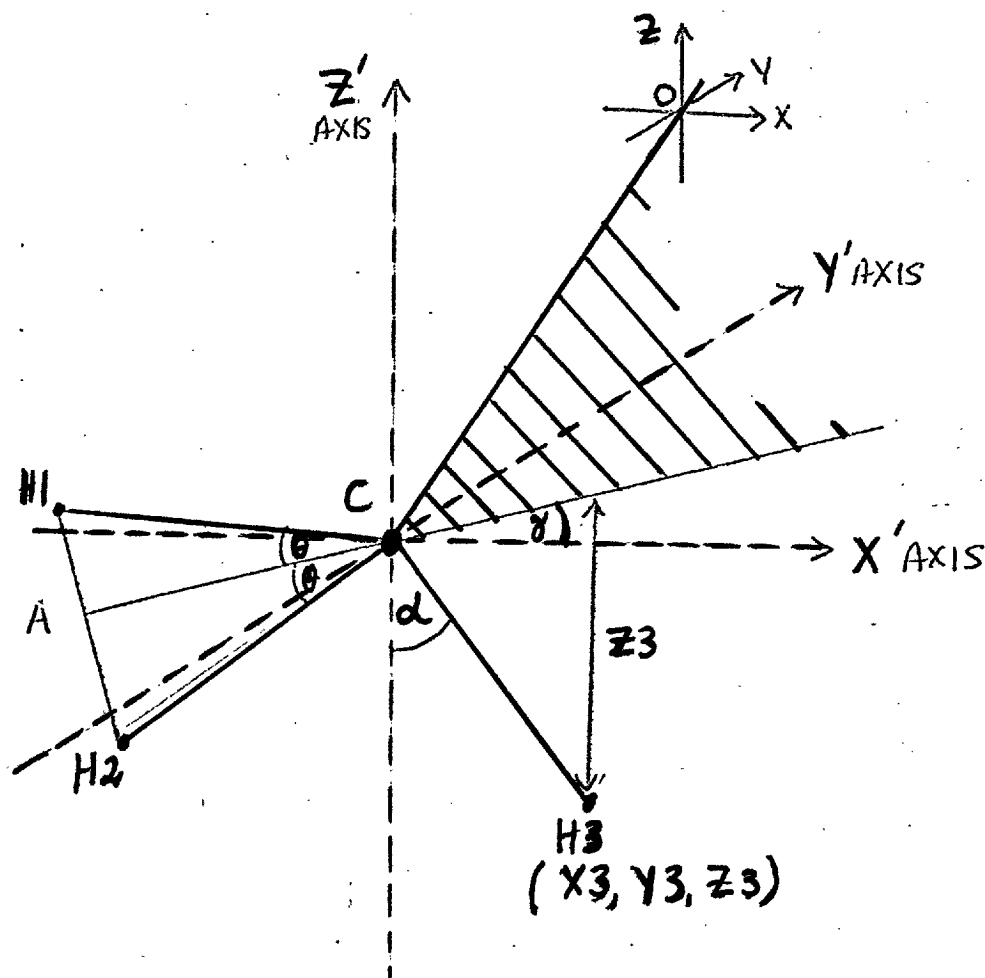


Fig. 4 (7) - Spatial orientation of methyl group.

4.12 Shifting from the vertical axis

It has been shown that it is generally thought that fatty acids crystals were displaced from the vertical. As shown in fig. 4(10) this will alter the co-ordinates X, Y, X1, X2, Y1, Y2, X3, Y3, and introduce the new co-ordinates Z1 and Z2. The adjacent Bottom layer is also tilted about the slip plane in the opposite direction.

When the chain is tilted about O, i.e. β , the co-ordinate ϕ increases to ϕ^1 where $p^1 = (MN + NO)$

$$\text{i.e. } p^1 = 0.77 \cos(\theta + \beta) + \left(\frac{DCH2}{2} + 0.77 \sin \theta\right) \sin \beta.$$

$$\text{Thus } X^1 = p^1 \cos \gamma \quad - (14)$$

$$\text{and } Y^1 = p^1 \sin \gamma \quad - (15)$$

i.e. When $\beta = 0$, — reduces to (1) and (2)

It can be shown that the co-ordinates X1, X2, Y1, Y2 are only affected by a $\cos \beta$ term and the X3, Y3, Z3 terms as follows.

$$X3 = HC \sin(\alpha + \beta) \cos \gamma \quad - (16)$$

$$Y3 = HC \sin(\alpha + \beta) \sin \gamma \quad - (17)$$

$$Z3 = HC \cos(\alpha + \beta) \quad - (18)$$

The new co-ords Z1 and Z2 are in fact equal to one another i.e.
 $Z1 = Z2 = HC \sin \beta$.

4.13 Parameters describing Internal rotation

The theory and applicability of the Internal Rotation of molecules was discussed in Chapter one. By examining fig. 4(11) it will be seen that two degrees of freedom of a methyl group are described.

By considering a straight rotation in the XY plane the parameter ROT is used to describe the angle rotated about C₁ in radians. By Newton's law when the shearing or dynamic process takes place any rotation will be accompanied by an equal and opposite one in the opposing layer. ROT will affect X1, Y1, X2, Y2, X3 and Y3 of the end group - it will also cause disturbances in methylene groups, but this only affects the total attractive energy slightly. The main consequence is to reduce the H-H repulsion contribution.

The second mode of rotation is described by ROCK. This causes a first order effect in repulsive potential, the second order effects of Z1 and Z2 were neglected. With these two parameters, rotations in the X, Y and Z directions may be described.

The complete co-ordinate system is now summarised.

$$\text{i.e. } X = (0.77 \cos(\theta + \beta)) + \left(\frac{DCH2}{2} + 0.77 \sin \theta \sin \beta\right) \cos \gamma \quad - (19)$$

$$Y = (0.77 \cos(\theta + \beta)) + \left(\frac{DCH2}{2} + 0.77 \sin \theta \sin \beta\right) \sin \gamma \quad - (20)$$

B		Y	A
(BBX(I) - X1) and (ABY(J) + Y1)		(ABX(I) + X1) and (ABY(J) + Y1)	Orientation B
(BAX(I) - X2) and (AAY(J) + Y2)		(AAX(I) + X2) and (AAY(J) + Y2)	Orientation A.
(BAX(I) - X2) and (CAY(J) - Y2)		(AAX(I) + X2) and (CAY(J) - Y2)	
(BBX(I) - X1) and (CBY(J) - Y1)		(ABX(I) + X1) and (CBY(J) - Y1)	
C			D

Fig. 4(8) CH summation array. Carbon of reference methyl group to top hydrogen molecules combined with array RZ01, on group ●(T) - ●(B).

B		Y	A
(BBXE(I) - X1 - X2) and (ABYE(J) - Y1 - Y2)		(ABXE(I) + X1 - X2) and (ABYE(J) - Y1 + Y2)	
BAXE(I) and AY(J)		AAXE(I) and AY(J)	X
BAXE(I) and CY(J)		AAXE(I) and CY(J)	
(BBXE(I) - X1 + X2) and (CBYE(J) + Y1 - Y2)		(ABXE(I) + X1 - X2) and (CBYE(J) + Y1 - Y2)	
C			D

Fig. 4(9) H1 molecule in source molecule to 'top' hydrogen molecules in bottom layer.

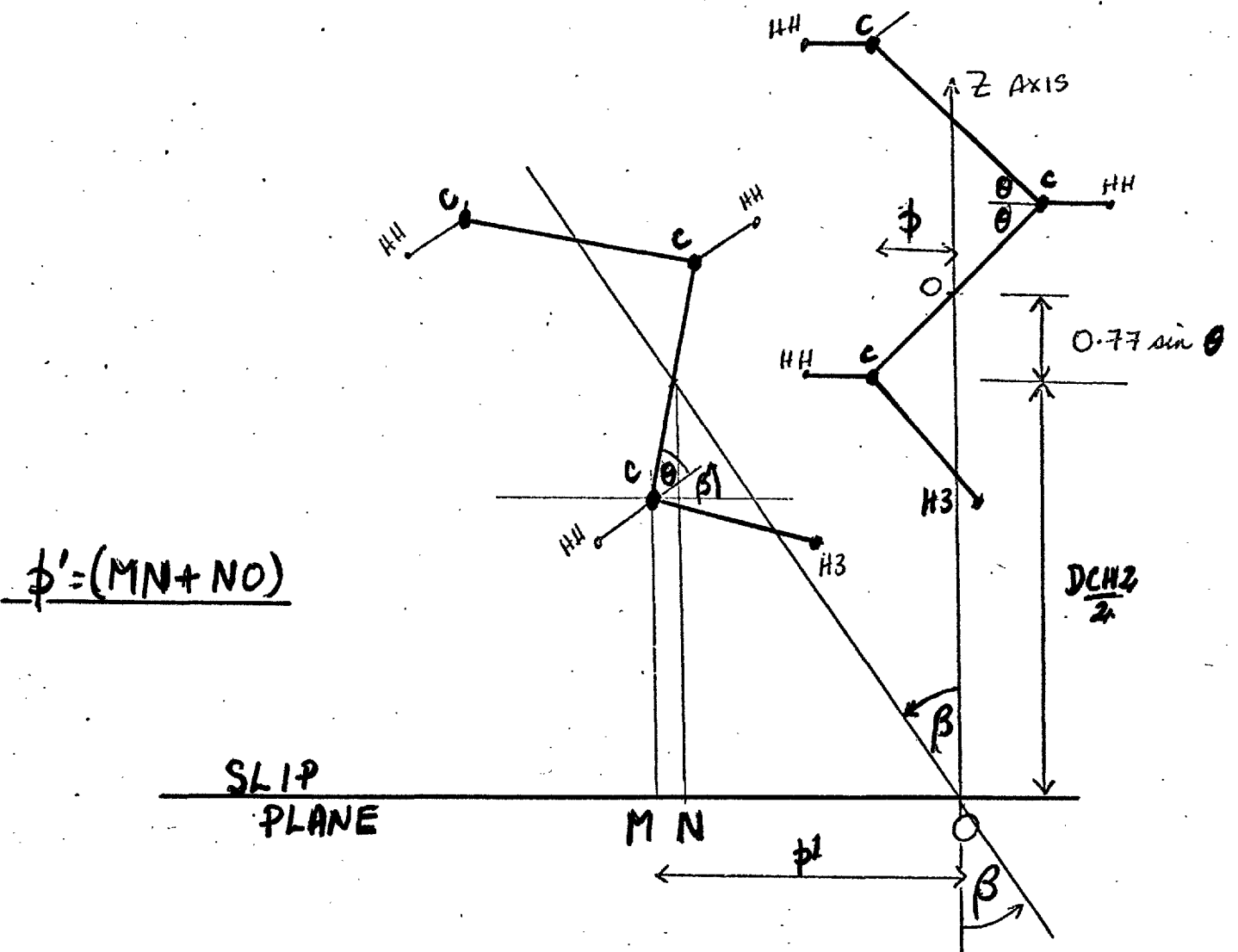


Fig. 4 (10) Effect of tilting the chain.

$$X1 = HC \cos (\theta - \gamma - ROT) \cos (\beta + ROCK) \quad - (21)$$

$$X2 = HC \cos (\theta + \gamma + ROT) \cos (\beta + ROCK) \quad - (22)$$

$$X3 = HC \cos (\gamma + ROT) \sin (\alpha + ROCK + \beta) \quad - (23)$$

$$Y1 = HC \sin (\theta - \gamma - ROT) \cos (\beta + ROCK) \quad - (24)$$

$$Y2 = HC \sin (\theta + \gamma + ROT) \cos (\beta + ROCK) \quad - (25)$$

$$Y3 = HC \sin (\gamma + ROT) \sin (\alpha + ROCK + \beta) \quad - (26)$$

$$Z1 = HC \sin \beta \quad - (27)$$

$$Z2 = HC \sin \beta \quad - (28)$$

$$Z3 = HC \cos (\alpha + ROCK + \beta) \quad - (29)$$

Where

- θ = half tetrahedral angle
- γ = setting angle
- β = Tilting of chain
- ROT = XY rotation

ROCK = Z rotation

α = angle of inclination of H3 to vertical.

HC = H - C bond distance.

4.14 Programing Method

The main program was split into a Main Program and four attractive subroutine (CC, CH, HH and Scattering Centres) computing inverse sixth distances and a repulsive subroutine. The potentials and output were then calculated in the main program. The computer used was a CDC 6600 and IBM 1794. - See fig. 4 (13)

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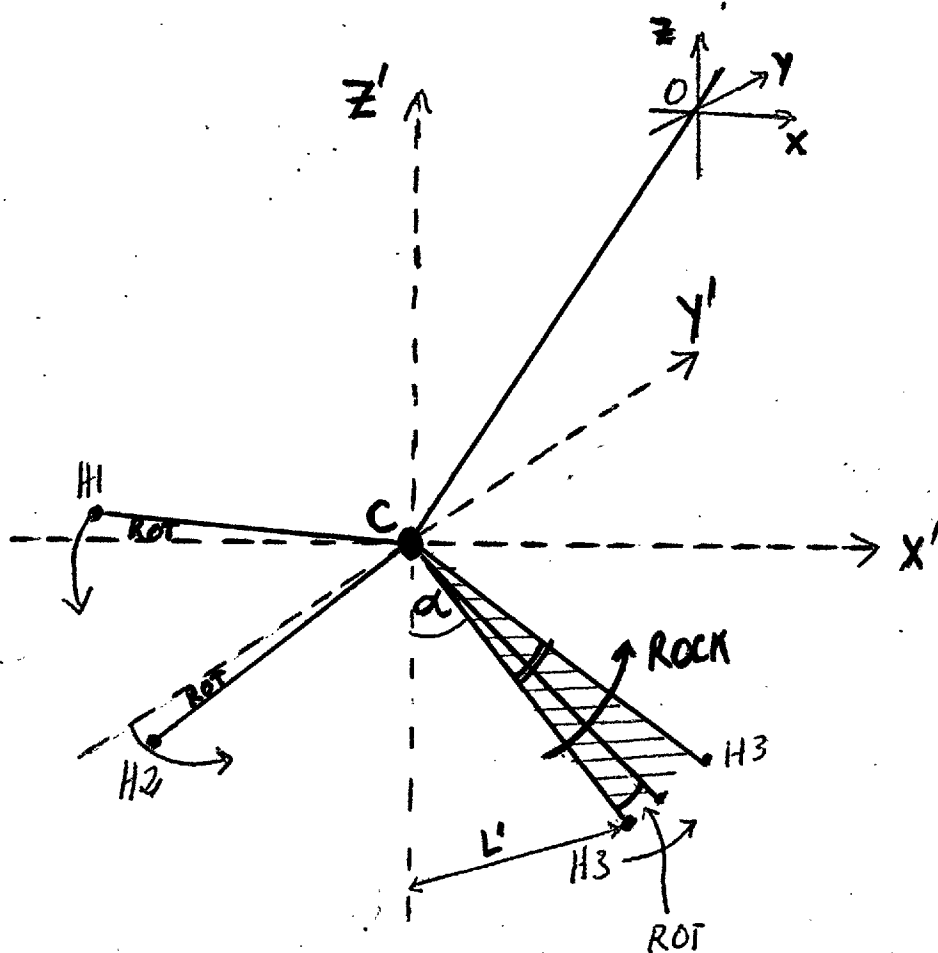


Fig. 4 (11) Internal Rotation of Methyl group.

\$IBFTC DRHH

SUBROUTINE RHH

C CALCULATION OF RELEVANT DISTANCES

INTEGER R,P,Q

COMMON AAX(12),ABX(12),BBX(12),BAX(12),AAXE(12),ABXE(12),BBXE(12),
1BAXE(12),AAXD(12),ABXD(12),BBXD(12),BAXD(12),AAY(15),ABY(15),CAY(15),
CBY(15),AY(15),CY(15),ABYE(15),Cbye(15),ABYV(15),CBYV(15),AAYD(15),
ABYD(15),CAYD(15),CBYD(15),RX(12),RY(15),RZE1(6),RZE2(6),RZO1(46),
RZO2(6),RZD1(6),CRIT,X1,X2,X3,Y1,Y2,Y3,SCCT,SCHT,SHHT,RP2(1200),
S,RP(1200),SCH2

N=0

DO 1 I=1,6,1

DO 2 J=1,8,1

RP2(N+1)=SQRT(RZO1(1)**2+(AAX(I)+X2+X1)**2+(AAY(J)-Y2+Y1)**2)
RP2(N+2)=SQRT(RZO1(1)**2+(BAX(I)-X2-X1)**2+(AAY(J)-Y2-Y1)**2)
RP2(N+3)=SQRT(RZO1(1)**2+(ABX(I)+X2+X1)**2+(ABY(J)-Y1-Y2)**2)
RP2(N+4)=SQRT(RZO1(1)**2+(BBX(I)-X2-X1)**2+(ABY(J)-Y1-Y2)**2)
RP2(N+5)=SQRT(RZO1(1)**2+(BBX(I)-X2-X1)**2+(CBY(J)+Y1+Y2)**2)
RP2(N+6)=SQRT(RZO1(1)**2+(ABX(I)+X2+X1)**2+(CBY(J)+Y1+Y2)**2)
RP2(N+7)=SQRT(RZO2(1)**2+(AAX(I)-X3+X1)**2+(AAY(J)-Y3-Y1)**2)
RP2(N+8)=SQRT(RZO2(1)**2+(ABX(I)-X3+X1)**2+(ABY(J)+Y3-Y1)**2)
RP2(N+9)=SQRT(RZO2(1)**2+(BAX(I)+X3-X1)**2+(AAY(J)-Y3-Y1)**2)
RP2(N+10)=SQRT(RZO2(1)**2+(BBX(I)+X3-X1)**2+(ABY(J)+Y3-Y1)**2)
RP2(N+11)=SQRT(RZO2(1)**2+(BBX(I)+X3-X1)**2+(CBY(J)-Y3+Y1)**2)
RP2(N+12)=SQRT(RZO2(1)**2+(ABX(I)-X3+X1)**2+(CBY(J)-Y3+Y1)**2)
RP2(N+13)=SQRT(RZO2(1)**2+(AAX(I)-X3+X2)**2+(AAY(J)-Y3+Y2)**2)
RP2(N+14)=SQRT(RZO2(1)**2+(ABX(I)-X3+X2)**2+(ABY(J)+Y3+Y2)**2)
RP2(N+15)=SQRT(RZO2(1)**2+(BAX(I)+X3-X2)**2+(AAY(J)-Y3+Y2)**2)
RP2(N+16)=SQRT(RZO2(1)**2+(BBX(I)+X3-X2)**2+(ABY(J)+Y3+Y2)**2)
RP2(N+17)=SQRT(RZO2(1)**2+(BBX(I)+X3-X2)**2+(CBY(J)-Y3-Y2)**2)
RP2(N+18)=SQRT(RZO2(1)**2+(ABX(I)-X3+X2)**2+(CBY(J)-Y3-Y2)**2)
RP2(N+19)=SQRT(RZO2(1)**2+(BAX(I)+X3-X1)**2+(CAY(J)+Y3+Y1)**2)
RP2(N+20)=SQRT(RZO2(1)**2+(AAX(I)-X3+X1)**2+(CAY(J)+Y3+Y1)**2)
RP2(N+21)=SQRT(RZO1(1)**2+(BAX(I)-X2-X1)**2+(CAY(J)-Y2+Y1)**2)
RP2(N+22)=SQRT(RZO1(1)**2+(AAX(I)+X2+X1)**2+(CAY(J)-Y2+Y1)**2)
RP2(N+23)=SQRT(RZO2(1)**2+(BAX(I)+X3-X2)**2+(CAY(J)+Y3-Y2)**2)
RP2(N+24)=SQRT(RZO2(1)**2+(AAX(I)-X3+X2)**2+(CAY(J)+Y3-Y2)**2)

N=N+24

2 CONTINUE

1 CONTINUE

C INEQUALITY TEST

DO 3 KA=1,1152,1

IF (RP2(KA).GT.6.0) GO TO 4

GO TO 3

4 RP2(KA)=4.0

3 CONTINUE

M=0

DO 5 I=1,6,1

DO 6 J=1,8,1

RP(M+1)=SQRT(RZO1(1)**2+(AAY(J)-Y1-Y1)**2+(AAX(I)+X1+X1)**2)
RP(M+2)=SQRT(RZO1(1)**2+(AAY(J)-Y1-Y1)**2+(BAX(I)-X1-X1)**2)
RP(M+3)=SQRT(RZO1(1)**2+(AAX(I)+X2+X2)**2+(AAY(J)+Y2+Y2)**2)
RP(M+4)=SQRT(RZO1(1)**2+(BAX(I)-X2-X2)**2+(AAY(J)+Y2+Y2)**2)
RP(M+5)=SQRT(RZO1(1)**2+(BAX(I)-X1-X1)**2+(CAY(J)+Y1+Y1)**2)
RP(M+6)=SQRT(RZO1(1)**2+(AAX(I)+X1+X1)**2+(CAY(J)+Y1+Y1)**2)
RP(M+7)=SQRT(RZO1(1)**2+(BAX(I)-X2-X2)**2+(CAY(J)-Y2-Y2)**2)
RP(M+8)=SQRT(RZO1(1)**2+(AAX(I)+X2+X2)**2+(CAY(J)-Y2-Y2)**2)
RP(M+9)=SQRT((BAX(I)+X3+X3)**2+(CAY(J)+Y3+Y3)**2+CRIT**2)
RP(M+10)=SQRT((AAX(I)-X3-X3)**2+(CAY(J)+Y3+Y3)**2+CRIT**2)

Fig. 4 (12) Repulsive Subroutine for Shear Program

```

RP(M+11)=SQRT((AAX(I)-X3-X3)**2+(AAY(J)-Y3-Y3)**2+CRIT**2)
RP(M+12)=SQRT((BAX(I)+X3+X3)**2+(AAY(J)-Y3-Y3)**2+CRIT**2)
RP(M+13)=SQRT(RZ01(1)**2+(ABX(I)+X1+X1)**2+ABY(J)**2)
RP(M+14)=SQRT(RZ01(1)**2+(ABX(I)+X1+X1)**2+CBY(J)**2)
RP(M+15)=SQRT(RZ01(1)**2+(BBX(I)-X1-X1)**2+ABY(J)**2)
RP(M+16)=SQRT(RZ01(1)**2+(BBX(I)-X1-X1)**2+CBY(J)**2)
RP(M+17)=SQRT((ABX(I)-X3-X3)**2+ABY(J)**2+CRIT**2)
RP(M+18)=SQRT((ABX(I)-X3-X3)**2+CBY(J)**2+CRIT**2)
RP(M+19)=SQRT((BBX(I)+X3+X3)**2+ABY(J)**2+CRIT**2)
RP(M+20)=SQRT((BBX(I)+X3+X3)**2+CBY(J)**2+CRIT**2)
RP(M+21)=SQRT((ABX(I)+X2+X2)**2+ABY(J)**2+RZ01(1)**2)
RP(M+22)=SQRT((ABX(I)+X2+X2)**2+CBY(J)**2+RZ01(1)**2)
RP(M+23)=SQRT((BBX(I)-X2-X2)**2+ABY(J)**2+RZ01(1)**2)
RP(M+24)=SQRT((BBX(I)-X2-X2)**2+CBY(J)**2+RZ01(1)**2)
M=M+24
6 CONTINUE
5 CONTINUE
C      INEQUALITY TEST
DO 7 KB=1,1152,1
  IF (RP(KB).GT.6.0) GO TO 8
  GO TO 7
8 RP(KB)=4.0
7 CONTINUE
  RETURN
  END

```

Fig. 4 (12) - continued

Continued from section 4.9

A displacement anywhere in Quadrant A can be achieved by

- (a) To the X arrays in Quadrant A and D, subtract $D \sin(MF)$
- (b) " " X " " " B " C, add $D \sin(MF)$
- (c) " " Y " " " C " D, add $D \cos(MF)$
- (d) " " Y " " " A " B, subtract $D \cos(MF)$

The algebra will then take care of any displacement in 360° .

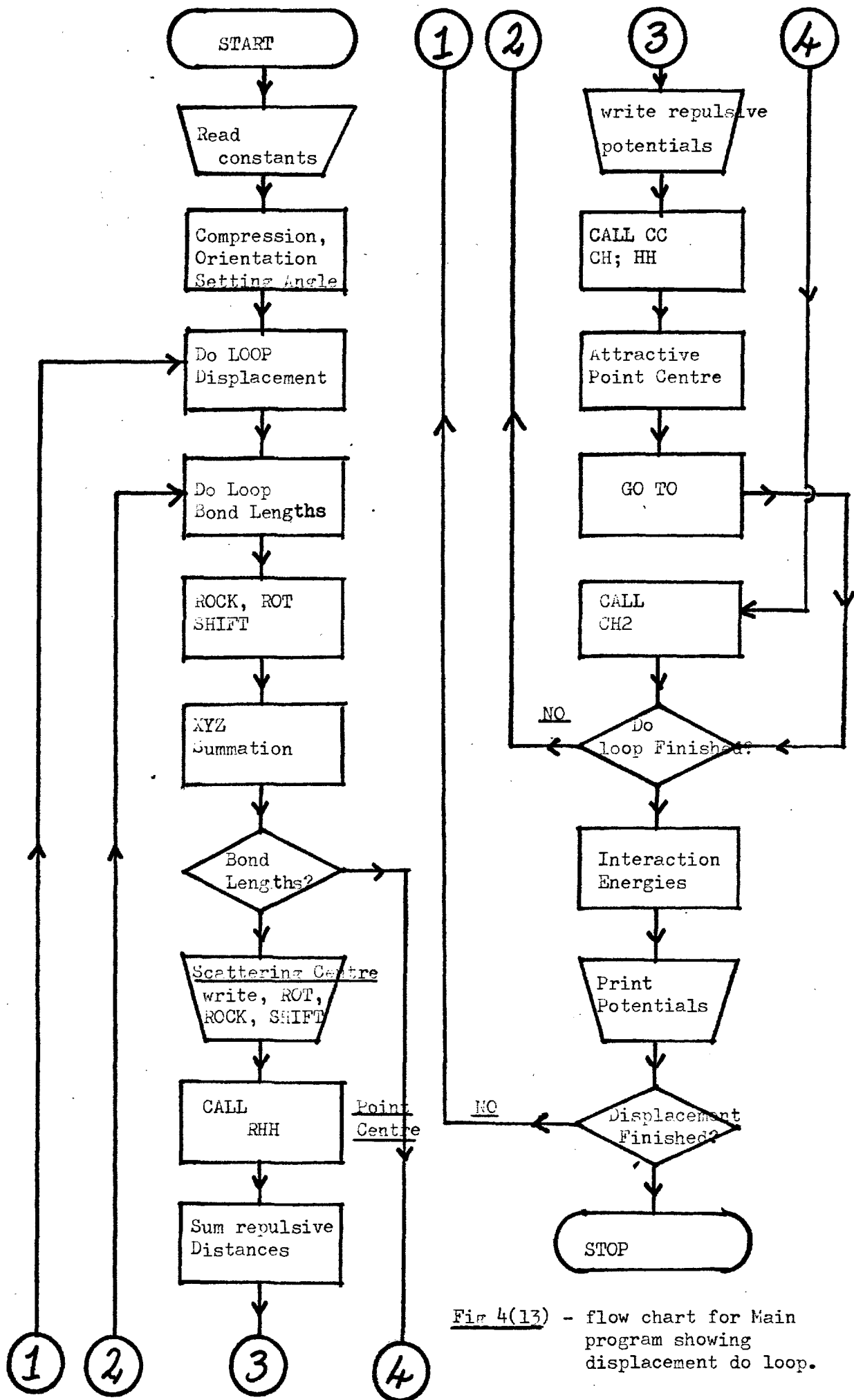


Fig 4(13) - flow chart for Main program showing displacement do loop.

CHAPTER 5 - CHECKING PROCEDURE

5.1 Boundary conditions of the Co-ordinate system

When all the computing errors of the co-ordinate system were dealt with the logic of the system was tested. The program was used to revolve the molecules in the equilibrium position about their Z axis by increasing the setting angle periodically from 0° to 360° in steps of 1° and printing out all the co-ordinates X, Y, X1, X2, Y1, Y2, X3, Y3, Z3.

The following results were obtained.

$\gamma = 0^\circ$

X = L, Y = 0, Z3 = 0.900341, X3 = L', Y3 = 0

$\gamma = 90^\circ$

X = 0, Y = L, Z3 = 0.900341, X3 = 0, Y3 = L'

$\gamma = 180^\circ$

X = -L, Y = 0, Z3 = 0.900341, X3 = -L', Y3 = 0

$\gamma = 270^\circ$

X = 0, Y = -L, Z3 = 0.900341, X3 = 0, Y3 = -L'

These fulfill the boundary conditions as stated in Chapter 4.

In addition by examining the equations for X1, X2, Y1, Y2 several sign changes are apparent by virtue of the relationships.

$$\cos(-\beta) = \cos \beta \quad \text{and} \quad \sin(-\beta) = -\sin(\beta)$$

i.e.

At $\gamma = 35^\circ 16'$ ($\theta + \alpha$) $\rightarrow 90$, $X2 < 0$, $Y2 > 0$

At $\gamma = 126^\circ 16'$ ($\theta + \alpha$) $\rightarrow 180$, $X2 < 0$, $Y2 < 0$

At $\gamma = 216^\circ 16'$ ($\theta + \alpha$) $\rightarrow 270$, $X2 > 0$, $Y2 < 0$

At $\gamma = 306^\circ 16'$ ($\theta + \alpha$) $\rightarrow 360$, $X2 > 0$, $Y2 > 0$

At $\gamma = 54^\circ 44'$ ($\theta - \alpha$) $\rightarrow 0$, $X1 > 0$, $Y1 < 0$

At $\gamma = 144^\circ 44'$ ($\theta - \alpha$) $\rightarrow -90$, $X1 < 0$, $Y1 < 0$

At $\gamma = 234^\circ 44'$ ($\theta - \alpha$) $\rightarrow -180$, $X1 < 0$, $Y1 > 0$

At $\gamma = 324^\circ 44'$ ($\theta - \alpha$) $\rightarrow -360$, $X1 > 0$, $Y1 > 0$

These results show the co-ords are internally consistent and if these are added and subtracted to the summation arrays consistently then the algebra will be correct. In some cases negative distances will arise but in the subroutines all the distances are squared. Checks were also carried out on all the Summation arrays - firstly to see if they were summing correctly and secondly to inspect the sums as a function of γ .

i.e. (i) $\cdot AAX(I) = CX + 2X + RX(I)$

$$\gamma = 0 - 3.662 \text{ \AA} + RX(I)$$

$$\gamma = 90^\circ - 2.773 \text{ \AA} + RX(I)$$

$$\begin{aligned} \delta &= 180 - 1.884 \text{ \AA} + \text{RX(I)} \\ \delta &= 270 - 2.773 \text{ \AA} + \text{RX(I)} \\ \text{(ii) } \text{CXYE(J)} &= \text{RY(J)} + \text{CY/2.0} - 2.0\text{Y} \\ \delta &= 0 - 2.478 \text{ \AA} + \text{RY(J)} \\ \delta &= 90 - 1.589 \text{ \AA} + \text{RY(J)} \\ \delta &= 180 - 2.478 \text{ \AA} + \text{RY(J)} \\ \delta &= 270 - 3.367 \text{ \AA} + \text{RY(J)} \end{aligned}$$

See figs 5(1) and 5 (2)

5.2 Boundary condition of rotations

Having shown the consistency of the individual distances the attractive subroutines CC and CH₂ were checked for symmetry as a function of Setting Angle. A program was run and by examination of the symmetry of the C-C bonding system in fig. 4(1) the sum of inverse sixths as a function of δ should be symmetrical. This is shown in fig. 5 (3); reaching a maximum at 180°. Similarly the subroutine CH is not symmetrical because of the influence of the H3 atom, nor is subroutine HH. All these subroutines were debugged and shown to process these properties. Again in all these cases the important boundary condition of continuity through 360° was shown. Fig. 5(4)

5.3 Displacement and Orientation over the cell

An extremely important property of the model is periodicity about the unit cell when the molecules are sheared over the methyl plane. Programs were run to displace the source molecule in steps of 0.25 Å along the X axis, Y axis and diagonal in Quadrant A. These should all be periodic from the property of the unit cell. Displacements were carried out over Quadrants B,C,D to test the algebra. By calculating the direction of shear accurately from the dimension of the cell-periodic displacement over 2,3 and 4 cells were shown. In all cases using all permutations of attractive and repulsive potentials for varying Setting Angles periodicity was established.

As far as computing technique applies care was taken to ensure that the same condition regarding force range and spatial distribution apply at all stages during displacement. Ideally this should be a sphere at what ever range is required round the source molecule. Unless this condition was applied periodicity could not be achieved. See figs 5(5), 5(6), 5(7), 5(8), 5(9), - for $\delta = 30^\circ$ and Barton Point centre potential.

5.4 Checking with Cameron's Model

A value of the Z distance between the H3 molecules was calculated and compared in Chapter 4 and close agreement was achieved. Cameron (1)

124X = -0.235548E 00,Y = 0.376958E 00,X1 = 0.423662E 00,Y1 = -0.101080E 01
X2 = -0.109423E 01,Y2 = 0.623263E-01,X3 = -0.331189E 00,Y3 = 0.530015E 00,Z3 = 0.900341E 00

125X = -0.242091E 00,Y = 0.372790E 00,X1 = 0.405957E 00,Y1 = -0.101804E 01
X2 = -0.109515E 01,Y2 = 0.432200E-01,X3 = -0.340388E 00,Y3 = 0.524154E 00,Z3 = 0.900341E 00

126X = -0.248561E 00,Y = 0.368508E 00,X1 = 0.388128E 00,Y1 = -0.102497E 01
X2 = -0.109573E 01,Y2 = 0.241005E-01,X3 = -0.349484E 00,Y3 = 0.518134E 00,Z3 = 0.900341E 00

127X = -0.254954E 00,Y = 0.364114E 00,X1 = 0.370180E 00,Y1 = -0.103159E 01
X2 = -0.109599E 01,Y2 = 0.497360E-02,X3 = -0.358474E 00,Y3 = 0.511955E 00,Z3 = 0.900341E 00

128X = -0.261270E 00,Y = 0.359609E 00,X1 = 0.352120E 00,Y1 = -0.103790E 01
X2 = -0.109591E 01,Y2 = -0.141548E-01,X3 = -0.367354E 00,Y3 = 0.505621E 00,Z3 = 0.900341E 00

129X = -0.267506E 00,Y = 0.354994E 00,X1 = 0.333953E 00,Y1 = -0.104388E 01
X2 = -0.109549E 01,Y2 = -0.332789E-01,X3 = -0.376122E 00,Y3 = 0.499133E 00,Z3 = 0.900341E 00

130X = -0.273661E 00,Y = 0.350271E 00,X1 = 0.315684E 00,Y1 = -0.104955E 01
X2 = -0.109475E 01,Y2 = -0.523928E-01,X3 = -0.384776E 00,Y3 = 0.492493E 00,Z3 = 0.900341E 00

131X = -0.279732E 00,Y = 0.345442E 00,X1 = 0.297319E 00,Y1 = -0.105490E 01
X2 = -0.109367E 01,Y2 = -0.714907E-01,X3 = -0.393312E 00,Y3 = 0.485702E 00,Z3 = 0.900341E 00

132X = -0.285718E 00,Y = 0.340507E 00,X1 = 0.278863E 00,Y1 = -0.105993E 01
X2 = -0.109225E 01,Y2 = -0.905670E-01,X3 = -0.401729E 00,Y3 = 0.478764E 00,Z3 = 0.900341E 00

133X = -0.291618E 00,Y = 0.335469E 00,X1 = 0.260322E 00,Y1 = -0.106464E 01
X2 = -0.109050E 01,Y2 = -0.109616E 00,X3 = -0.410024E 00,Y3 = 0.471680E 00,Z3 = 0.900341E 00

Fig. 5(1) Print out showing co-ordinates X, Y, X1, Y1, X2, Y2, X3, Y3, and Z3 From $\delta = 124^\circ$ to 133°

EXECUTION

2 SCCT = 0.164996E-02

AAX = 0.366200E 01 0.110880E 02 0.185140E 02
 ABX = 0.737500E 01 0.148010E 02 0.222270E 02
 BAX = 0.376400E 01 0.111900E 02 0.186160E 02
 BBX = 0.510050E-01 0.747700E 01 0.149030E 02
 AAXE = 0.277300E 01 0.101990E 02 0.176250E 02
 ABXE = 0.648600E 01 0.139120E 02 0.213380E 02
 BBXE = 0.940000E 00 0.836600E 01 0.157920E 02
 BAXE = 0.465300E 01 0.120790E 02 0.195050E 02
 AAXD = 0.188400E 01 0.931000E 01 0.167360E 02
 ABXD = 0.559700E 01 0.130230E 02 0.204490E 02
 BAXD = 0.554200E 01 0.129680E 02 0.203940E 02
 BBXD = 0.182900E 01 0.925500E 01 0.166810E 02
 CBYE = 0.247800E 01 0.743400E 01 0.123900E 02 0.173460E 02
 ABYE = 0.247800E 01 0.743400E 01 0.123900E 02 0.173460E 02
 AAY = 0.000000E-38 0.495600E 01 0.991200E 01 0.148680E 02
 CAY = 0.495600E 01 0.991200E 01 0.148680E 02 0.198240E 02
 ABY = 0.247800E 01 0.743400E 01 0.123900E 02 0.173460E 02
 ABYD = 0.247800E 01 0.743400E 01 0.123900E 02 0.173460E 02
 AAYD = -0.000000E-38 0.495600E 01 0.991200E 01 0.148680E 02
 CAYD = 0.495600E 01 0.991200E 01 0.148680E 02 0.198240E 02

7 SCCT = 0.164891E-02

AAX = 0.365862E 01 0.110846E 02 0.185106E 02
 ABX = 0.737162E 01 0.147976E 02 0.222236E 02
 BAX = 0.376738E 01 0.111934E 02 0.186194E 02
 BBX = 0.543829E-01 0.748038E 01 0.149064E 02
 AAXE = 0.277300E 01 0.101990E 02 0.176250E 02
 ABXE = 0.648600E 01 0.139120E 02 0.213380E 02
 BBXE = 0.940000E 00 0.836600E 01 0.157920E 02
 BAXE = 0.465300E 01 0.120790E 02 0.195050E 02
 AAXD = 0.188738E 01 0.931338E 01 0.167394E 02
 ABXD = 0.560038E 01 0.130264E 02 0.204524E 02
 BAXD = 0.553862E 01 0.129646E 02 0.203906E 02
 BBXD = 0.182562E 01 0.925162E 01 0.166776E 02
 CBYE = 0.240052E 01 0.735652E 01 0.123125E 02 0.172685E 02
 ABYE = 0.255548E 01 0.751148E 01 0.124675E 02 0.174235E 02
 AAY = 0.774814E-01 0.503348E 01 0.998948E 01 0.149455E 02
 CAY = 0.487852E 01 0.983452E 01 0.147905E 02 0.197465E 02
 ABY = 0.247800E 01 0.743400E 01 0.123900E 02 0.173460E 02
 ABYD = 0.247800E 01 0.743400E 01 0.123900E 02 0.173460E 02

Fig. 5(2) Part of print out - checking summation arrays as a function of Setting Angle.

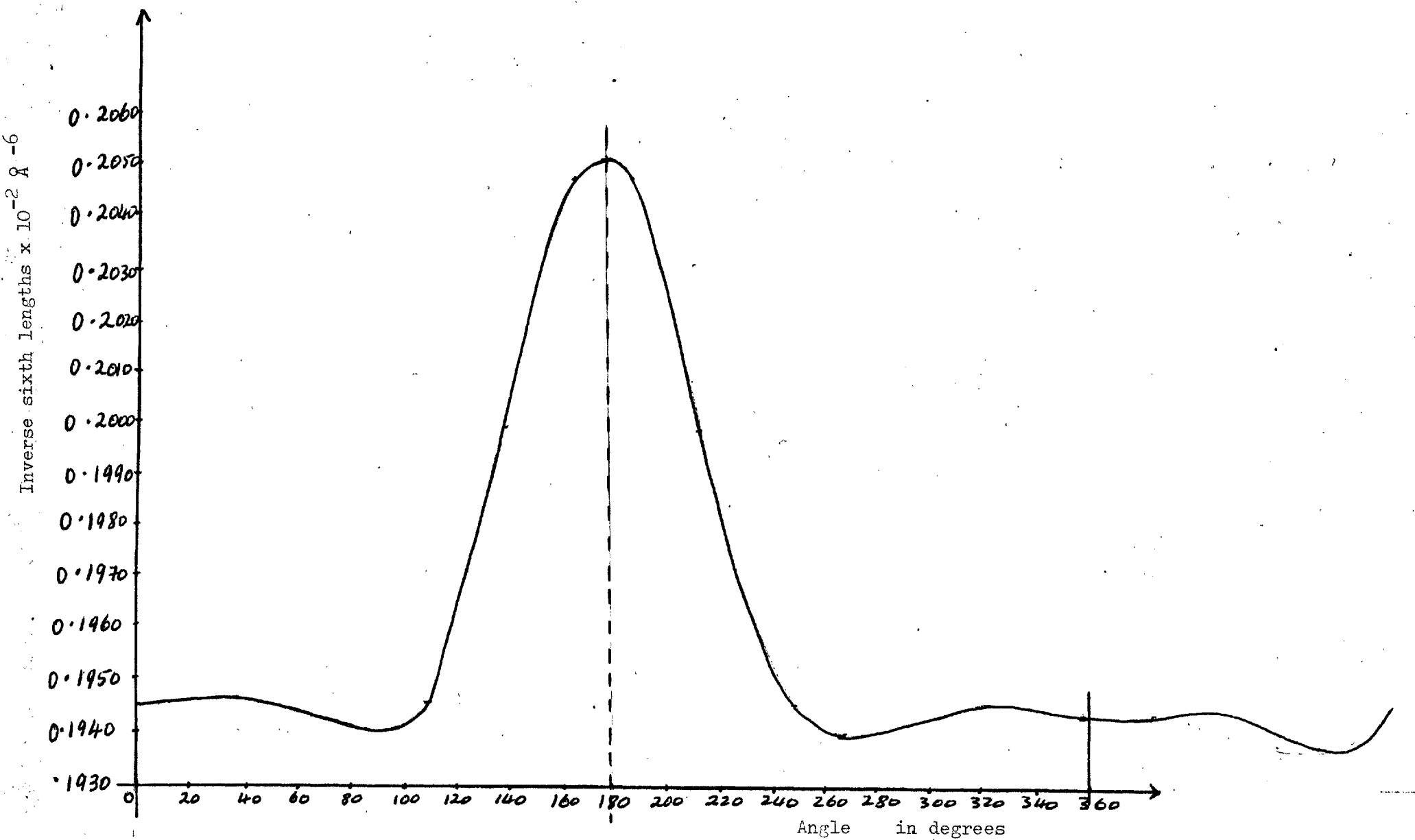


Fig. 5(3) Sum of inverse sixth distance of CC length as a function of Setting Angle

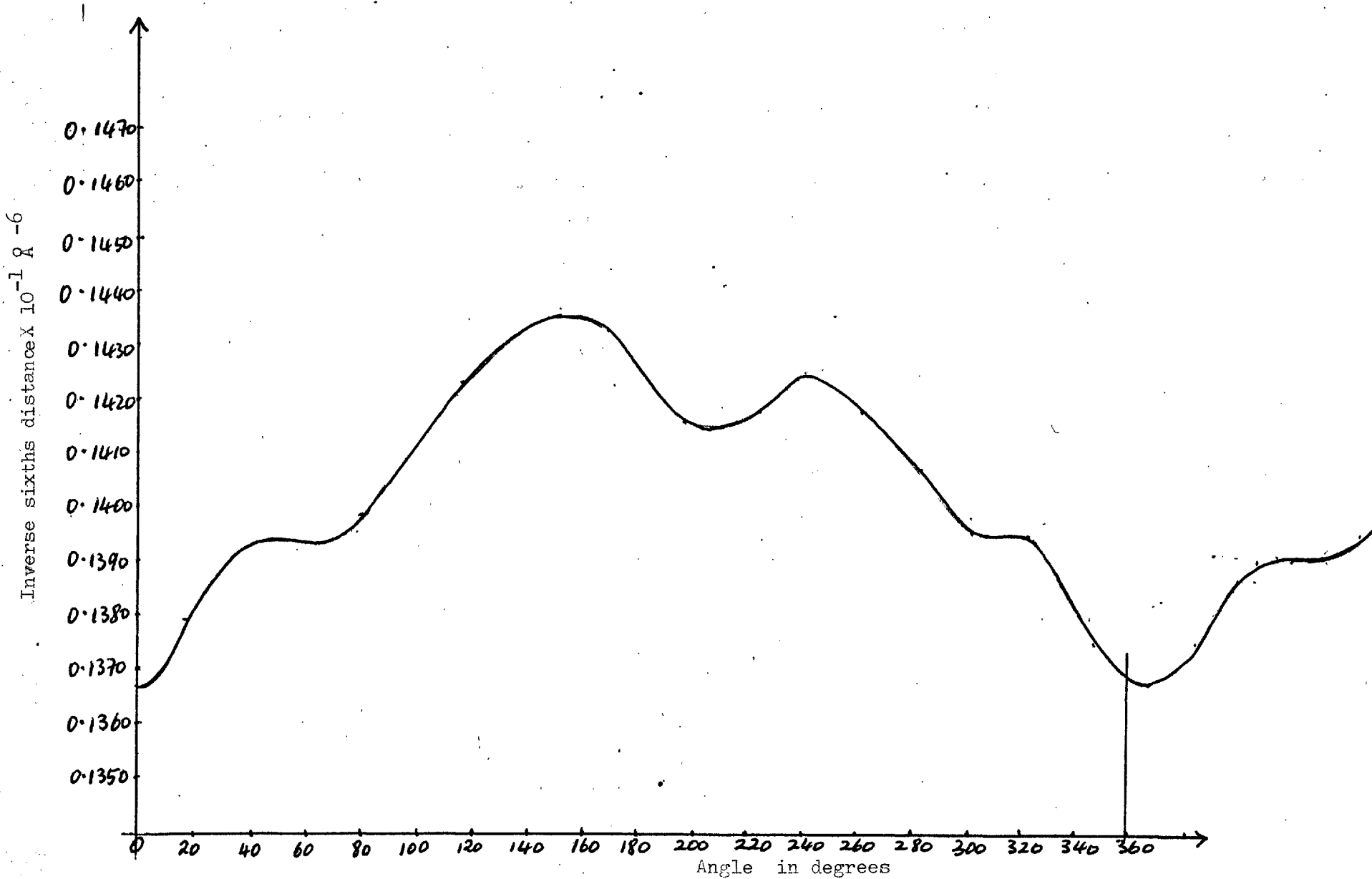


Fig. 5 (4) Inverse sixth distances for CH lengths as a function of Setting Angle.

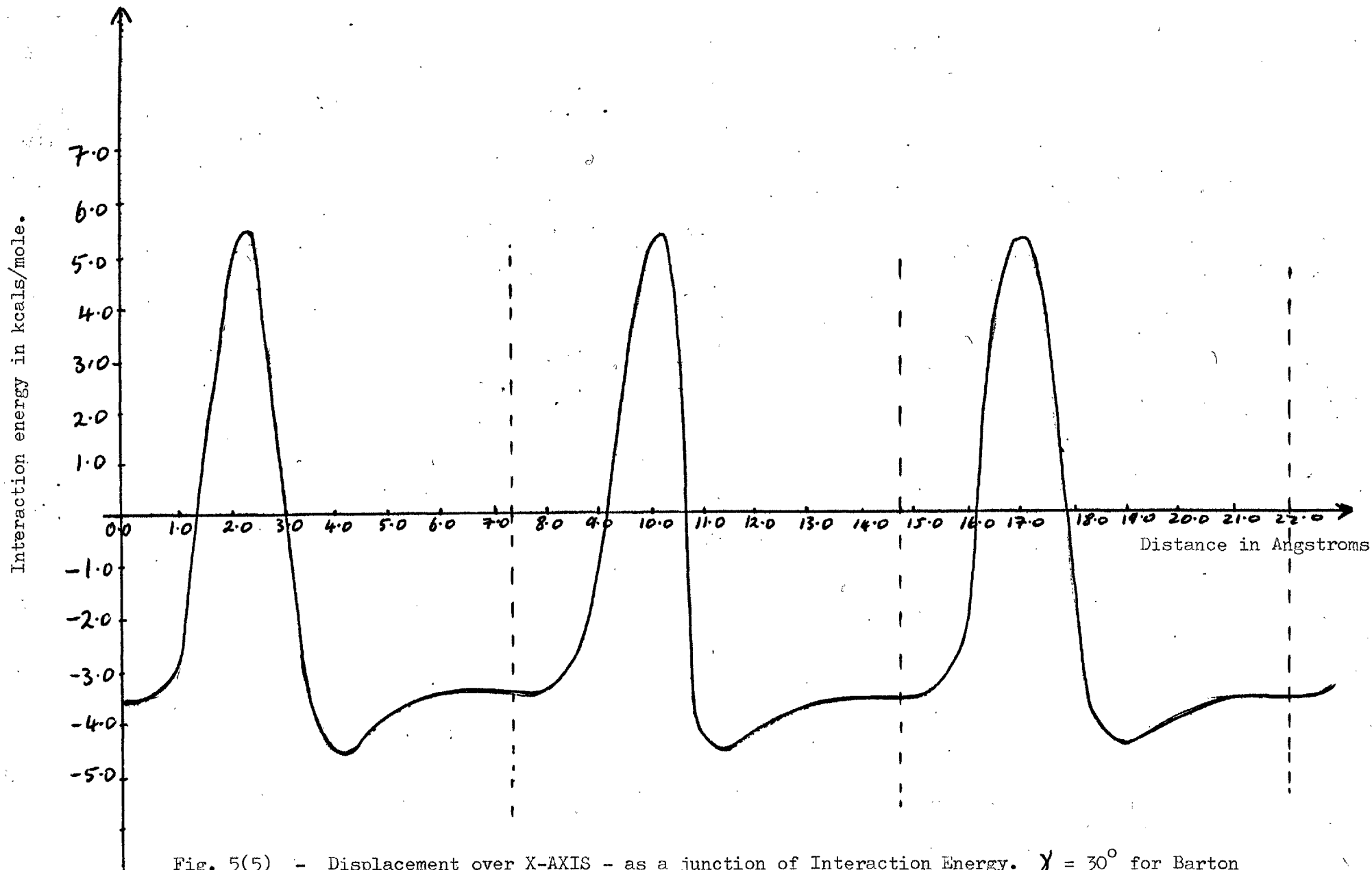


Fig. 5(5) - Displacement over X-AXIS - as a junction of Interaction Energy. $\gamma = 30^\circ$ for Barton point centre potential

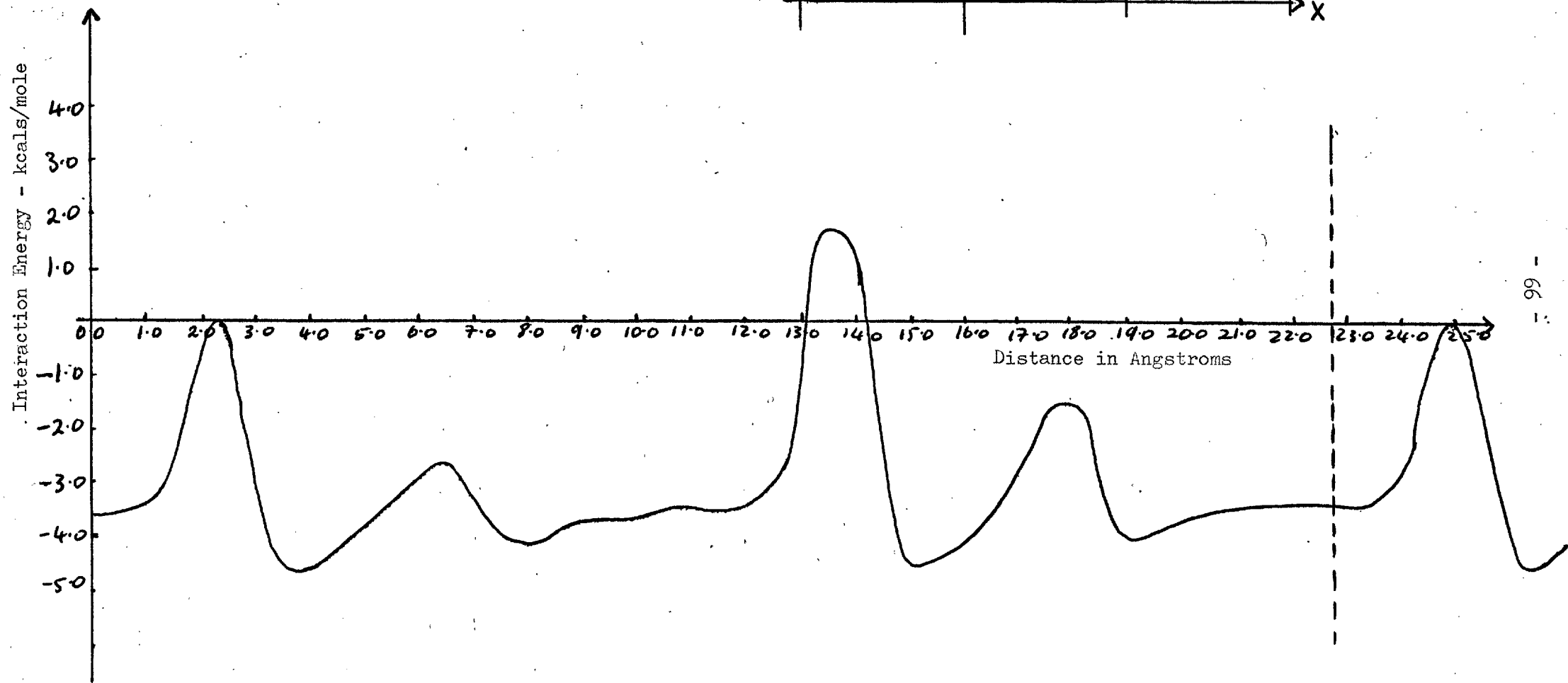


Fig. 5(6) Displacement over 3 unit cells at an angle of 13°

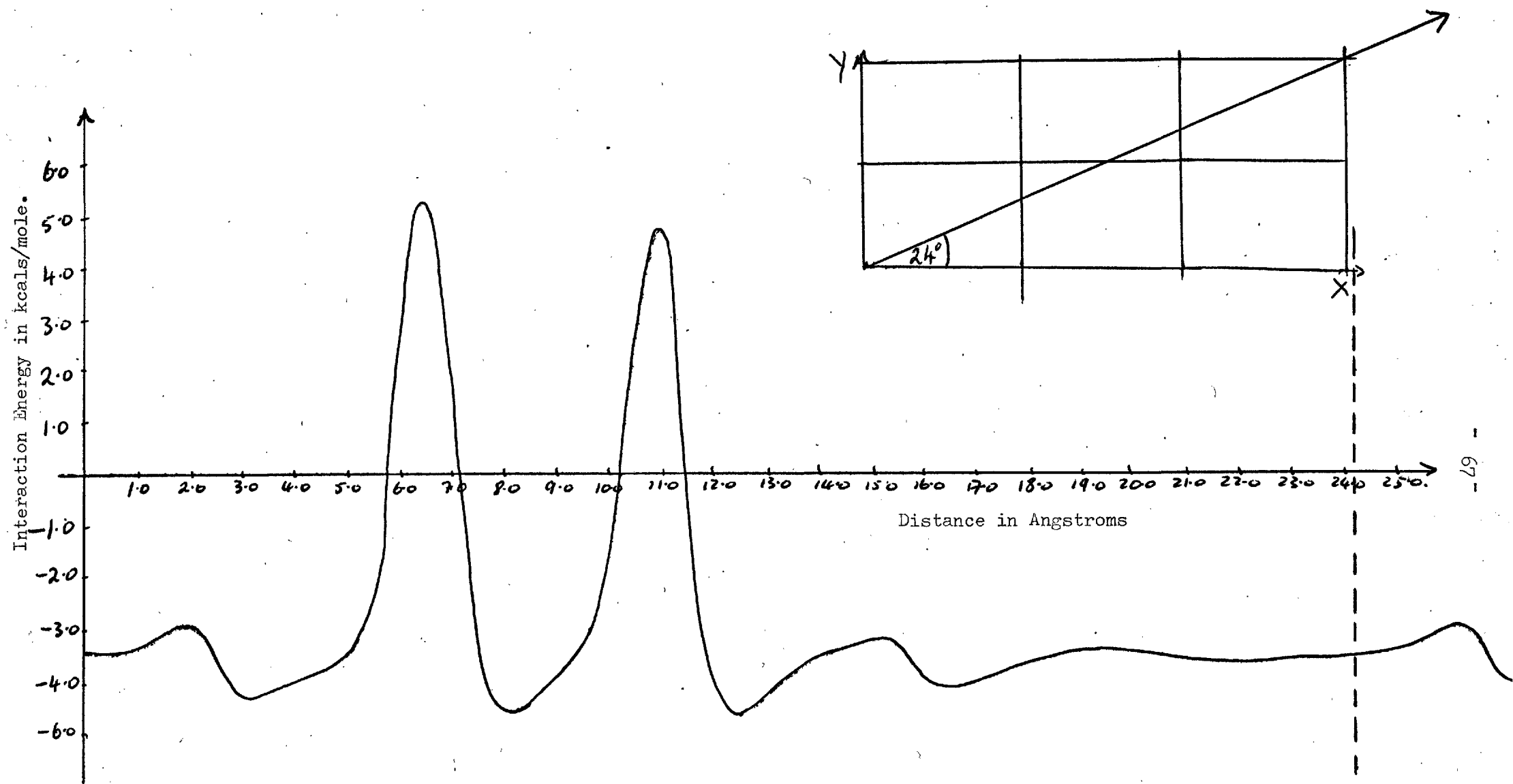


Fig. 5(7) - Displacement at an angle of 24°

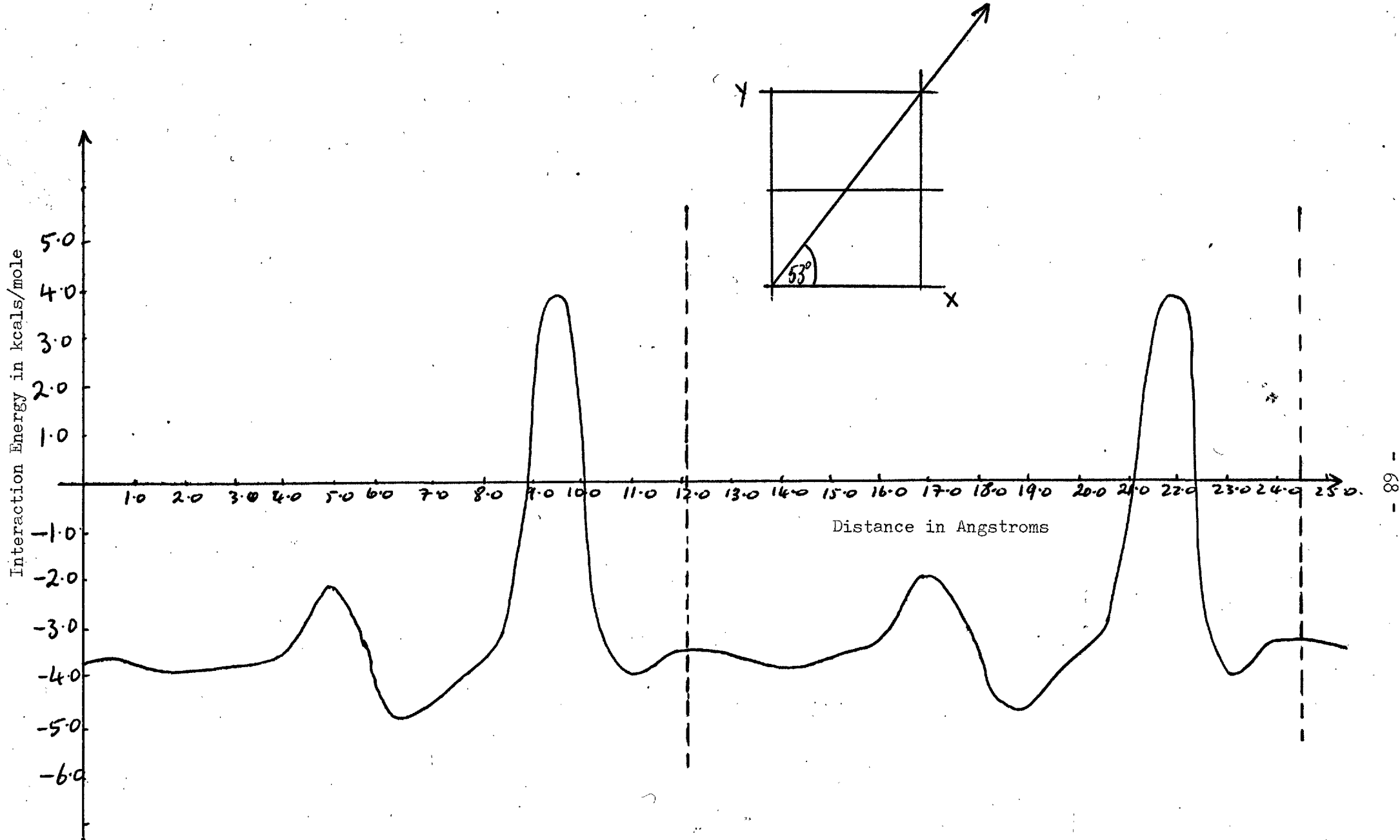


Fig. 5(8) Displacement at an angle of 53°

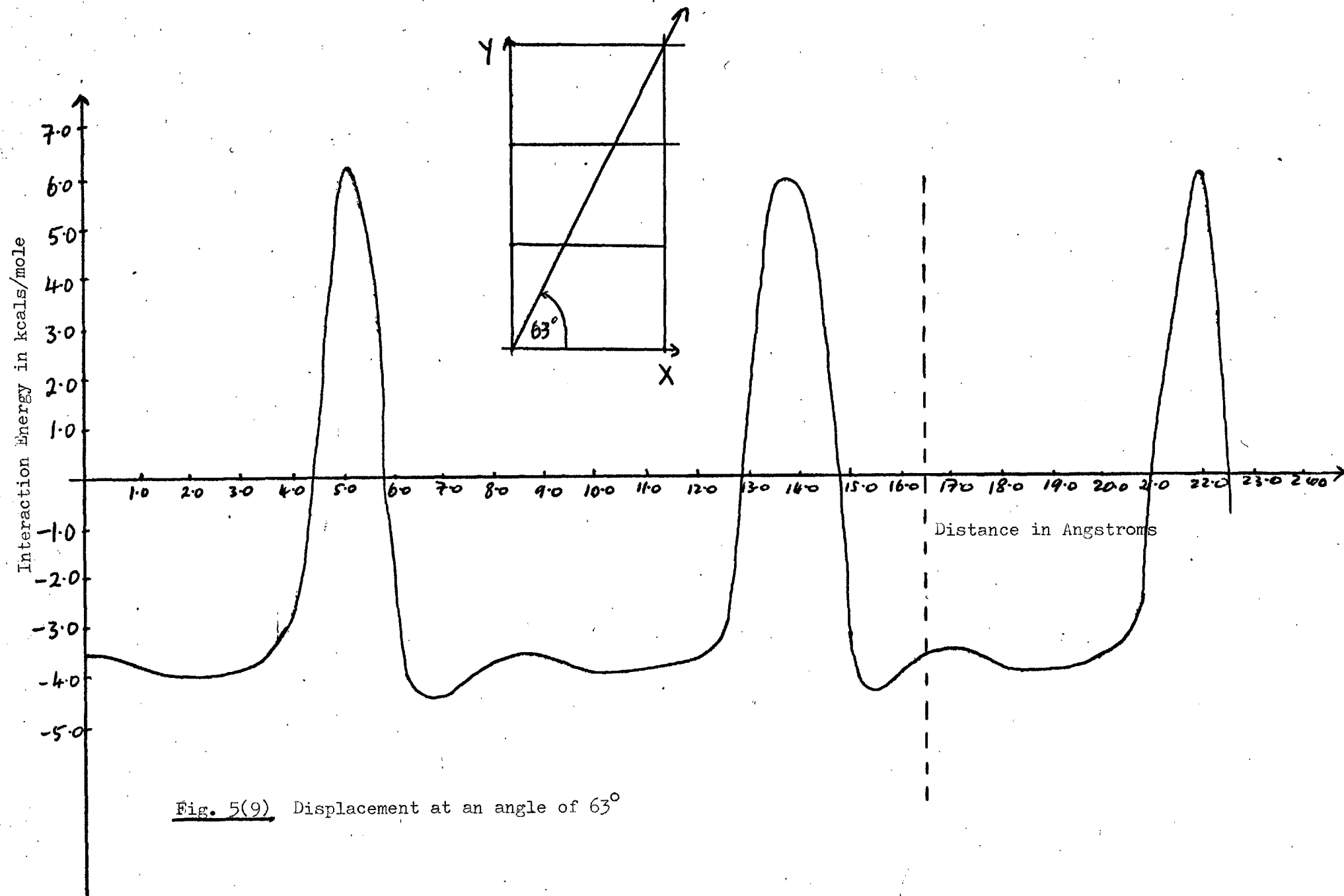


Fig. 5(9) Displacement at an angle of 63°

assumed an angle of 30° from Müller and after calculating attractive scattering centres distances, Broeder (2) criticized this value and states it is 30% down if a London-Polanyi integration method is used. Cameron only used a range of 8 Å. When a computed range of 25-30 Å was used which to all practical purposes is an infinite range using Cameron's assumptions of $\gamma = 30^\circ$, and using the attractive centre attractive potential, a value of $1.7825 \times 10^{-3} \text{ cm}^{-6}$ was obtained which is 32% larger than Cameron's value.

Also a comparison with Cameron's value under compression can be made although not precisely the same conditions were used. A program to compute results at DCH2 = 3.09 Å, 2.85 Å, 2.65 Å and 2.45 Å corresponding to Cameron external loads of zero, 40, 80, and 120 tons/sq.inch was run with $\gamma = 44^\circ$. E, is using a Slater Scattering Centre potential system.

pressure	DCH2 (Å)	Cameron kcal/mole	E, (Computed)
i.e. 0	3.09	1.2	1.36
40	2.85	1.52	1.388
80	2.65	1.93	1.652
120	2.45	2.29	1.979

Cameron states the nearest H-H distances at equilibrium are 2.58 Å and 3.15 Å (two pairs each). When the repulsive arrays were printed out as a function of γ the nearest H-H distances at $\gamma = 30$ were 2.582 Å, 3.07 Å (two pairs each) and 2.782 Å.

5.5 Program to calculate Setting Angle.

The Setting Angle parameter γ , as shown in diagrams in the previous chapter is a very important fixed quantity of hydrocarbon crystals. Cameron(1) used Muller's (3) computed figure of 30° but more recently a figure of $48 \pm 5^\circ$ is experimentally shown by Smith (4) for $C_{21}H_{24}$ to $C_{29}H_{60}$. The angle refers to the minimum energy of the crystal i.e. the equilibrium energy which is a function of the angle γ . To derive it theoretically the minimum energy of a CH_2 group with respect to its own layer is found. Ideally the sphere of influence from the chosen molecule should include only scattering centres, but this is clearly an impossibility for fatty acids, due to the polar carboxyl group and the methyl end group. Also near the end groups the next adjacent layer will act also. But it will be shown that these objections are only second order effects and they only alter the magnitude of the energies involved not the minimum.

The program was calculated using the same principles as before but using fig. 5(10) to construct the summation arrays instead of fig. 4(1) i.e. a single methylene radical as source point with respect to its immediate neighbours instead of a single chain with respect to the next layer.

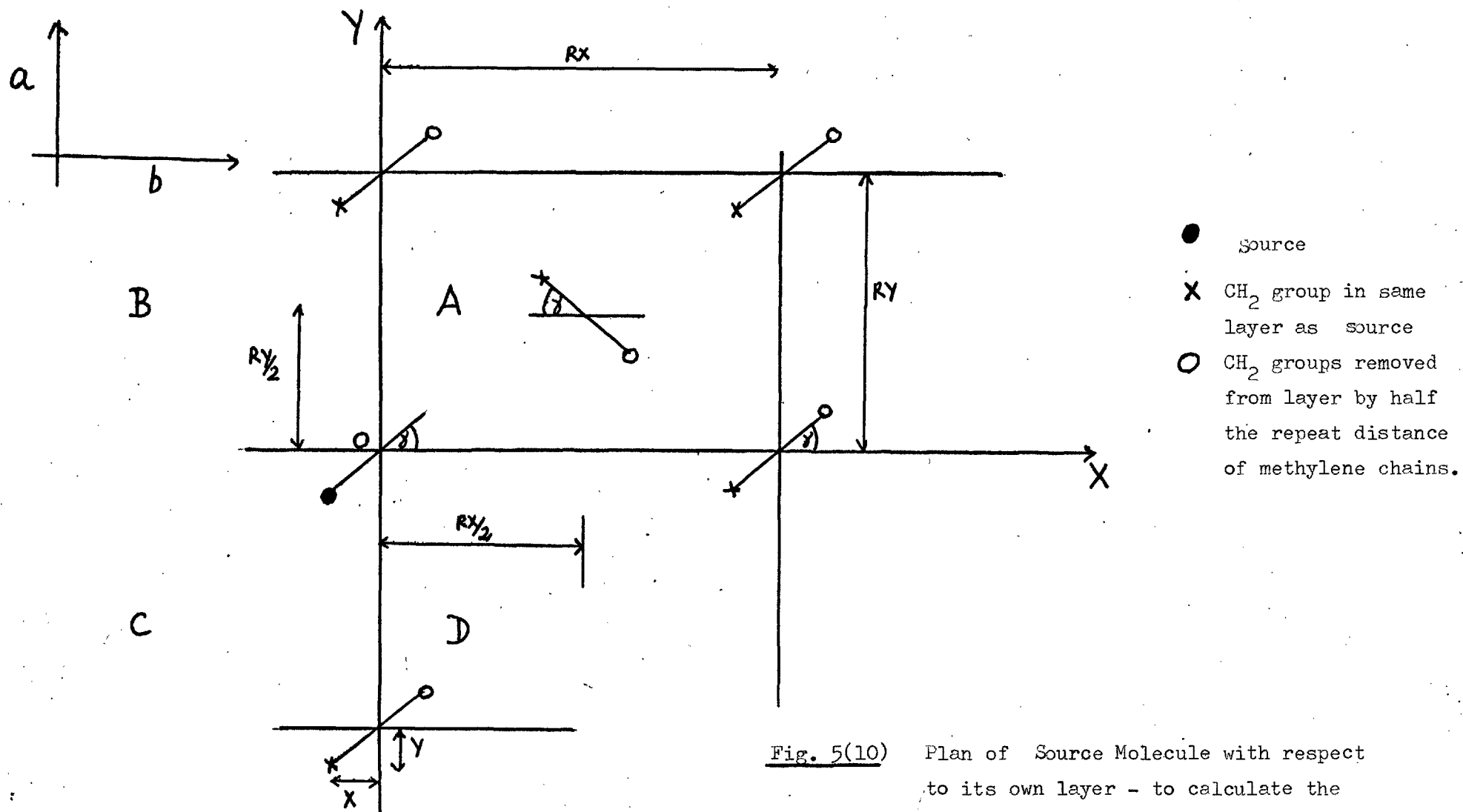


Fig. 5(10) Plan of Source Molecule with respect to its own layer - to calculate the Setting Angle.

The Summation Arrays were as follows.

$$\begin{aligned} \text{AAX (I)} &= \text{RX(I)} \\ \text{ABX(I)} &= \text{RX/2} + \text{RX(I)} \\ \text{AAY(J)} &= \text{RY(J)} \\ \text{ABY(J)} &= \text{RY/2} + 2\text{Y} + \text{RY(J)} \\ \text{CBY(J)} &= \text{RY/2} - 2\text{Y} + \text{RY(J)} \end{aligned}$$

These were all the radicals in the same plane as the source and by introducing Z arrays based on the repeat distance all the distances could be computed in accordance with fig 4(3).

Also summation arrays for the remaining layers were introduced as follows.

$$\begin{aligned} \text{AAXO(I)} &= 2\text{X} + \text{RX(I)} \\ \text{ABXO(I)} &= \text{RX/2} + \text{RX(I)} + 2\text{X} \\ \text{AAYO(J)} &= 2\text{Y} + \text{RY(J)} \\ \text{ABYO(J)} &= \text{CY/2} + \text{RY(J)} \\ \text{BAXO(I)} &= \text{RX} - 2\text{X} + \text{RX(I)} \\ \text{BBXO(I)} &= \text{RY/2} + 2\text{X} + \text{RX(I)} \\ \text{CAYO(J)} &= \text{RY} - 2\text{Y} + \text{RY(J)} \end{aligned}$$

The repulsive distances were compounded using nearest neighbour distances from the summation arrays and co-ordinates X1, X2, Y1, Y2.

The new program consisted of the main deck, an attractive and repulsive subroutine.

All the results of all the potential combinations were printed out as a function of δ in steps of one degree. See fig. 5(11) and 5(12).

5.6 Results and Conclusions of Setting Angle Program

When the different potentials were plotted it was found that although the magnitude of the interaction curves differed, due to the large variety in repulsive potentials, they were all symmetrical about 180° and they all gave a minimum at $44 \pm 1^\circ$ which agrees within experimental error of Smith's (4) results.

In fig. 5(13) the results using Barton's repulsive potential are plotted showing a clear minimum at 44° and a mean difference between maximum and minimum of 1.8 kcals/mole. By examining fig. 5(3) (Attractive sum of inverse sixth as a function of Setting Angle for adjacent layers) it is seen that the profile up to 90° hardly alters. When the total interaction energy (repulsive plus scattering centre attraction potentials) of the top layer with respect to the bottom layer is plotted as a function of δ - it is found that the results do not affect the minimum energy at 44° - i.e. second order effect.

C

MAIN PROGRAM

- 73 -

PROGRAM SETT(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)

DIMENSION SET(500),ABA(2)

COMMON RX(5),RY(7),ABX(5),ABY(7),CBY(7),AAXO(5),ABXO(5),ABYO(7),BA
 1XO(5),BRXO(5), CAYO(7),AAYO(7),RZE(6),RZO(6),SET1,ODD(16),E
 3V4(12),EV2(4),X1,X2,Y1,Y2
 READ (5,1010) THETA,HC,CX,CY,BUK1,BART,A0,CON,EPG,BUK4,BTLL,BMUL,C
 1MUL,BSL,CSL,ECH2,(RZE(M),M=1,6),(RZO(L),L=1,6),(RX(I),I=1,5),(RY(J
 2),J=1,7)

1010 FORMAT (10X,F12.6)

DO 7000 K=2,462,30

SET(K-1)=FLOAT(K-2)*3.14159/180.0

DATA (ABA(JI),JI=1,2)/0.4445,0.6940/

DO 8000 JI=1,2

AB=ABA(JI)

X=AB*COS(SET(K-1))

Y=AB*SIN(SET(K-1))

X1=HC*COS(THETA-SET(K-1))

Y1=HC*SIN(THETA-SET(K-1))

X2=HC*COS(THETA+SET(K-1))

Y2=HC*SIN(THETA+SET(K-1))

DO 71 I=1,5

ABX(I)=RX(I)+CX/2.0

AAXO(I)=2.0*X+RX(1)

ABXO(I)=CX/2.0+2.0*X+RX(I)

BAXO(I)=CX-2.0*X+RX(1)

BBXO(I)=CX/2.0-2.0*X+RX(I)

71 CONTINUE

DO 400 I=1,5,1

IF (ABX(I).GT.25.0) ABX(I)=10000.0

IF (AAXO(I).GT.25.0) AAXO(I)=10000.0

IF (ABXO(I).GT.25.0) ABXO(I)=10000.0

IF (BAXO(I).GT.25.0) BAXO(I)=10000.0

IF (BBXO(I).GT.25.0) BBXO(I)=10000.0

400 CONTINUE

DO 81 J=1,7,1

ABY(J)=CY/2.0+2.0*Y+RY(J)

CBY(J)=CY/2.0-2.0*Y+RY(J)

AAYO(J)=2.0*Y+RY(J)

ABYO(J)=CY/2.0+RY(J)

CAYO(J)=CY-2.0*Y+RY(J)

81 CONTINUE

DO 401 J=1,7,1

IF (ABY(J).GT.25.0) ABY(J)=10000.0

IF (CBY(J).GT.25.0) CBY(J)=10000.0

IF (AAYO(J).GT.25.0) AAYO(J)=10000.0

IF (ABYO(J).GT.25.0) ABYO(J)=10000.0

IF (CAYO(J).GT.25.0) CAYO(J)=10000.0

401 CONTINUE

IF (AB.EQ.0.4445) GO TO 104

IF (AB.EQ.0.6940) GO TO 105

104 CONTINUE

C CALL REPULSIVE SUBROUTINE

CALL RHH

C CALCULATE REPULSIVE ENERGIES

SUM1=0.0

SUM4=0.0

SUM5=0.0

Fig. 5(11) - Setting Angle Program

```
SUM6=0.0
DO 7001 KI=1,16,1
E11=BUK1*EXP(-BART*ODD(KI)/AO)*CON*2.0
SUM1=SUM1+E11
E14=BUK4*EXP(-BTLL*ODD(KI)/AO)*CON*2.0
SUM4=SUM4+E14
E15=BIUL*EXP(-CMUL*ODD(KI)/AO)*CON*2.0
SUM5=SUM5+E15
E16=BSL*EXP(-CSL*ODD(KI)/AO)*ERG*2.0
SUM6=SUM6+E16
```

7001 CONTINUE

```
SU1=0.0
SU4=0.0
SU5=0.0
SU6=0.0
DO 7002 KJ=1,12,1
E21=BUK1*EXP(-BART*EV4(KJ)/AO)*CON*4.0
SU1=SU1+E21
E24=BUK4*EXP(-BTLL*EV4(KJ)/AO)*CON*4.0
SU4=SU4+E24
E25=BMUL*EXP(-CMUL*EV4(KJ)/AO)*CON*4.0
SU5=SU5+E25
E26=BSL*EXP(-CSL*EV4(KJ)/AO)*ERG*4.0
SU6=SU6+E26
```

7002 CONTINUE

```
S1=0.0
S4=0.0
S5=0.0
S6=0.0
DO 7003 KL=1,8,1
E31=BUK1*EXP(-BART*EV2(KL)/AO)*CON*2.0
S1=S1+E31
E34=BUK4*EXP(-BTLL*EV2(KL)/AO)*CON*2.0
S4=S4+E34
E35=BMUL*EXP(-CMUL*EV2(KL)/AO)*CON*2.0
S5=S5+E35
E36=BSL*EXP(-CSL*EV2(KL)/AO)*ERG*2.0
S6=S6+E36
```

7003 CONTINUE

C***** TOTAL REPULSIVE POTENTIALS

```
R1=SUM1+SU1+S1
R4=SUM4+SU4+S4
R5=SUM5+SU5+S5
R6=SUM6+SU6+S6
GO TO 8000
```

C CALL ATTRACTIVE SUBROUTINE

105 CONTINUE

```
CALL CH2
GO TO 8000
```

8000 CONTINUE

C SUM INTERACTION ENERGIES

```
ESKB=R1-ECH2*SET1
ESKBT=R4-ECH2*SET1
ESKM=R5-ECH2*SET1
ESKSL=R6-ECH2*SET1
WRITE (6,1000) K,SET1,R1,R4,R5,R6,ESKB,ESKBT,ESKM,ESKSL
```

```
1000 FORMAT (1X,I3,8H SET1 = ,E13.6,6H R1 = ,E13.6,6H R4 = ,E13.6,6H R5
1 = ,E13.6,6H R6 = ,E13.6,6H ESKB = ,E13.6,9H ESKBT = ,E13.6,9H
2ESKM = ,E13.6,9H ESKSL = ,E13.6,9H)
```

7000 CONTINUE

STOP

END

3 SET1 = .390674E-02 R1 = .240886E+00 R4 = .803337E+00 R5 = .612757E+00 R6 = .328751E+00
 ESKB = -.208363E+01 ESKBT = -.152118E+01 ESKM = -.171176E+01 ESKSL = -.199576E+01

.124467E-02 .320274E-04 .109932E-04 .160483E-03 .177686E-02 .257545E-04 .642770E-04 .380794E-03

4 SET1 = .389937E-02 R1 = .232262E+00 R4 = .778868E+00 R5 = .588190E+00 R6 = .317007E+00
 ESKB = -.208786E+01 ESKBT = -.154126E+01 ESKM = -.173193E+01 ESKSL = -.200312E+01

.124917E-02 .320274E-04 .109932E-04 .160483E-03 .175605E-02 .259517E-04 .635032E-04 .390538E-03

SET(43)

5 SET1 = .389222E-02 R1 = .226475E+00 R4 = .761485E+00 R5 = .572423E+00 R6 = .309120E+00
 ESKB = -.208940E+01 ESKBT = -.155439E+01 ESKM = -.174345E+01 ESKSL = -.200675E+01

.125364E-02 .320274E-04 .109932E-04 .160483E-03 .173529E-02 .261545E-04 .627547E-04 .400470E-03

SET(44)

6 SET1 = .388532E-02 R1 = .223522E+00 R4 = .751194E+00 R5 = .565434E+00 R6 = .305085E+00
 ESKB = -.208824E+01 ESKBT = -.156057E+01 ESKM = -.174633E+01 ESKSL = -.200668E+01

.125809E-02 .320274E-04 .109932E-04 .160483E-03 .171439E-02 .263631E-04 .620307E-04 .410585E-03

7 SET1 = .387846E-02 R1 = .223407E+00 R4 = .748003E+00 R5 = .567245E+00 R6 = .304910E+00
 ESKB = -.208428E+01 ESKBT = -.155968E+01 ESKM = -.174044E+01 ESKSL = -.200278E+01

.126249E-02 .320274E-04 .109932E-04 .160483E-03 .169380E-02 .265775E-04 .613307E-04 .420878E-03

8 SET1 = .387209E-02 R1 = .226143E+00 R4 = .751921E+00 R5 = .577924E+00 R6 = .308609E+00
 ESKB = -.207775E+01 ESKBT = -.155197E+01 ESKM = -.172597E+01 ESKSL = -.199529E+01

.126686E-02 .320274E-04 .109932E-04 .160483E-03 .167334E-02 .267977E-04 .606540E-04 .431343E-03

Fig. 5(12) - Print out showing minimum interaction energies

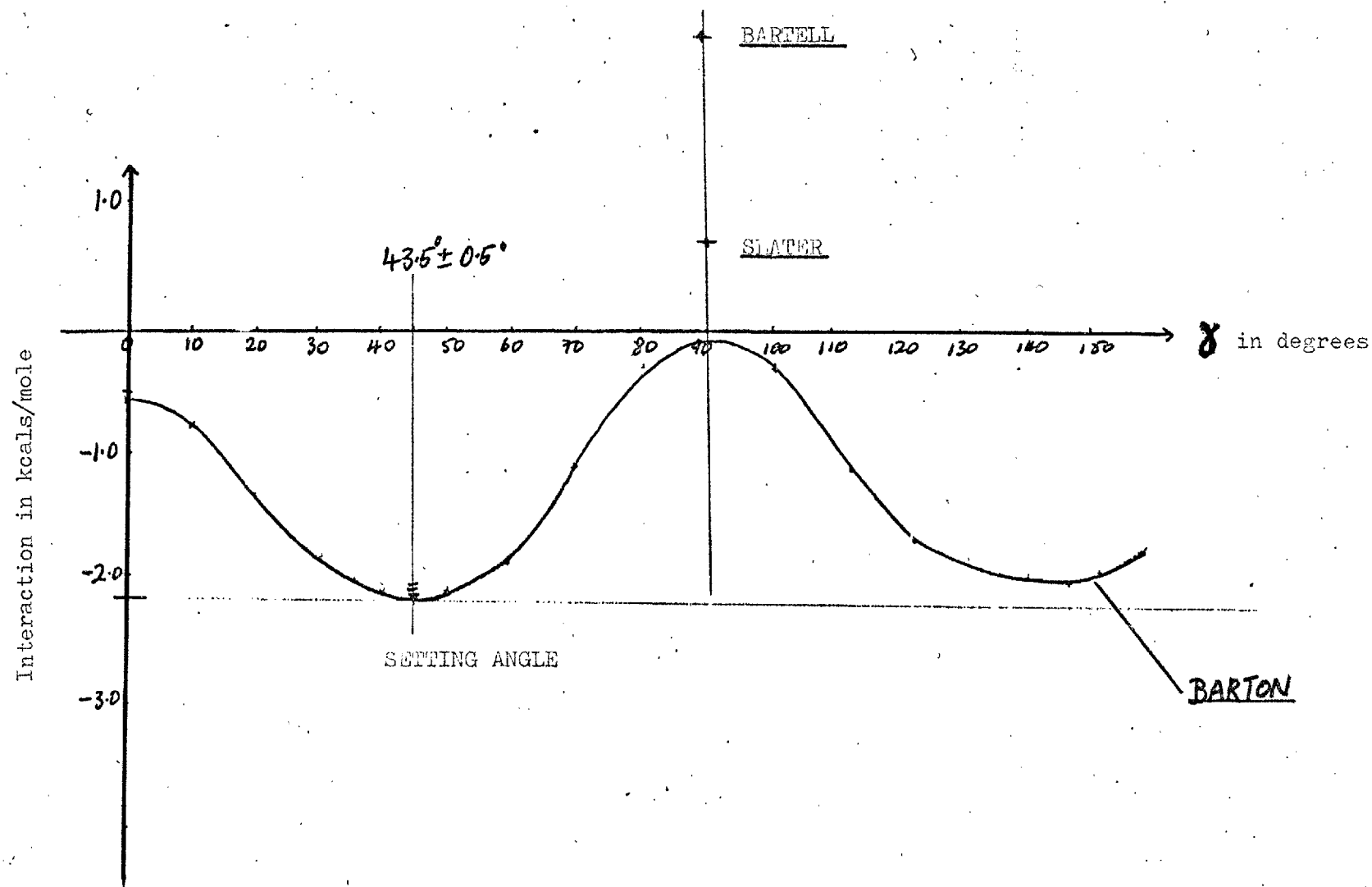


Fig. 5(13) - Distribution of Interaction Energy with γ showing Setting Angle

The magnitude of the energy at the minimum corresponds experimentally with the sublimation energy (because the energy of CH_2 groups is essentially the lattice energy) Akhmatov (5) gives this value as 2.3 kcal/mole/ CH_2 group. From all the results plotted the average of this value was found to 2.1 kcal/mole/ CH_2 group.

From the graphs it is possible to gauge an idea of the rigidity of the molecules in crystals. i.e. Using fig. 5(13) and assuming 12 carbon in a chain gives a value between maximum and minimum of 36.0 kcal/mole/CHAIN over a range of approximately 45° . From the shape of the graph; to rotate the chain 5° about the Z axis requires 0.8 kcal/mole. When the first program is sheared over the X-AXIS using a change of angle of $\pm 5^\circ$ from 45° the resultant change in the potential profile of the appropriate potential is only 0.6 kcal/mole. This trend is extended to a larger extent if harder potentials are used or larger changes of setting angle variation. Fig. 7(1)

Hence it must be concluded that rotations about the Z axis in paraffin or fatty crystals to reduce potential barriers is a second order effect compared to other mechanisms described later. However as described in Chapter Two only comparisons can be made and undoubtedly small rotations will occur ($1 - 3^\circ$) under certain circumstances. Also as described by Akhmatov (6) free rotation at room temperature must be a very rare phenomenon.

5.7 Compression of crystals in XY directions

An important content of methylene chains and crystals is their compressibilities and Muller (3) shows that the value of Young's Modulus along the Z axis is one order of magnitude higher than in the X and Y axis.

The Setting angle program was adapted to represent compression in the XY directions. (The X and Y compression of the Main program describing adjacent layers was found to be reliable) with respect to its own layer. By inspection of the diagrams of the model it is hard to imagine the X and Y compressibilities being equal because of the inequality of the cell dimension. The results of two programs describing compression in the XY directions are reproduced in figs. 5(14) and 5(15) for $\gamma = 44^\circ$.

It can be seen that although both give compressibility of the right magnitude the X direction has the steeper gradient. Programs for $\gamma = 30^\circ$ were also run and resulted in larger magnitudes in both directions. It is a very interesting fact that X-AXIS $\gamma(44)$ results are very nearly equal to (30) Y-AXIS results, when realising that the ratio of RX to RY is nearly equal to the ratio of 44 to 30. This suggests that for Muller's results to hold the cell should be square and γ be equal to 45° . See figs. 5(16) and 5(17).

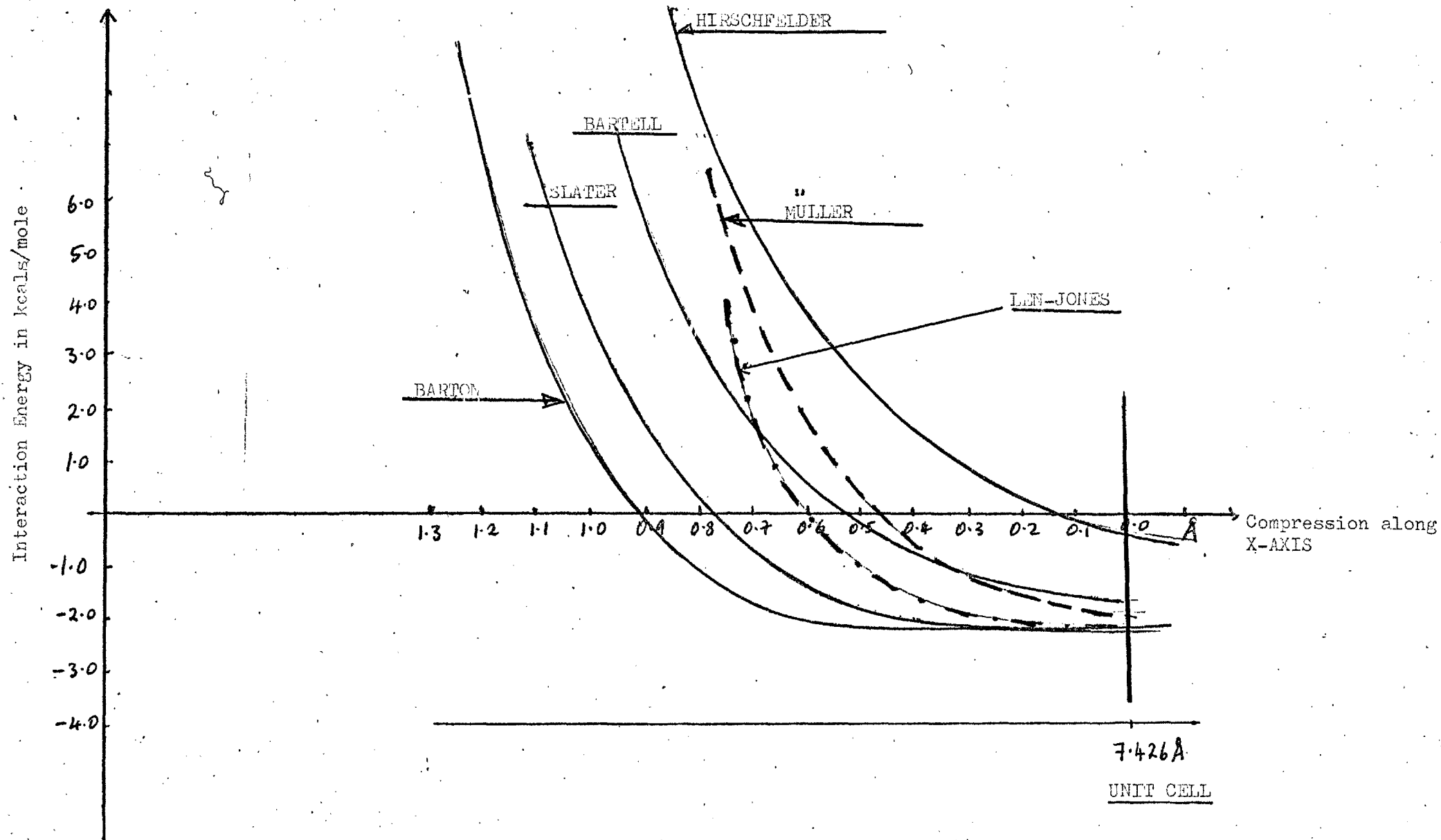


Fig. 5(14) Compression in X direction using 'Setting Program' - 8(44)

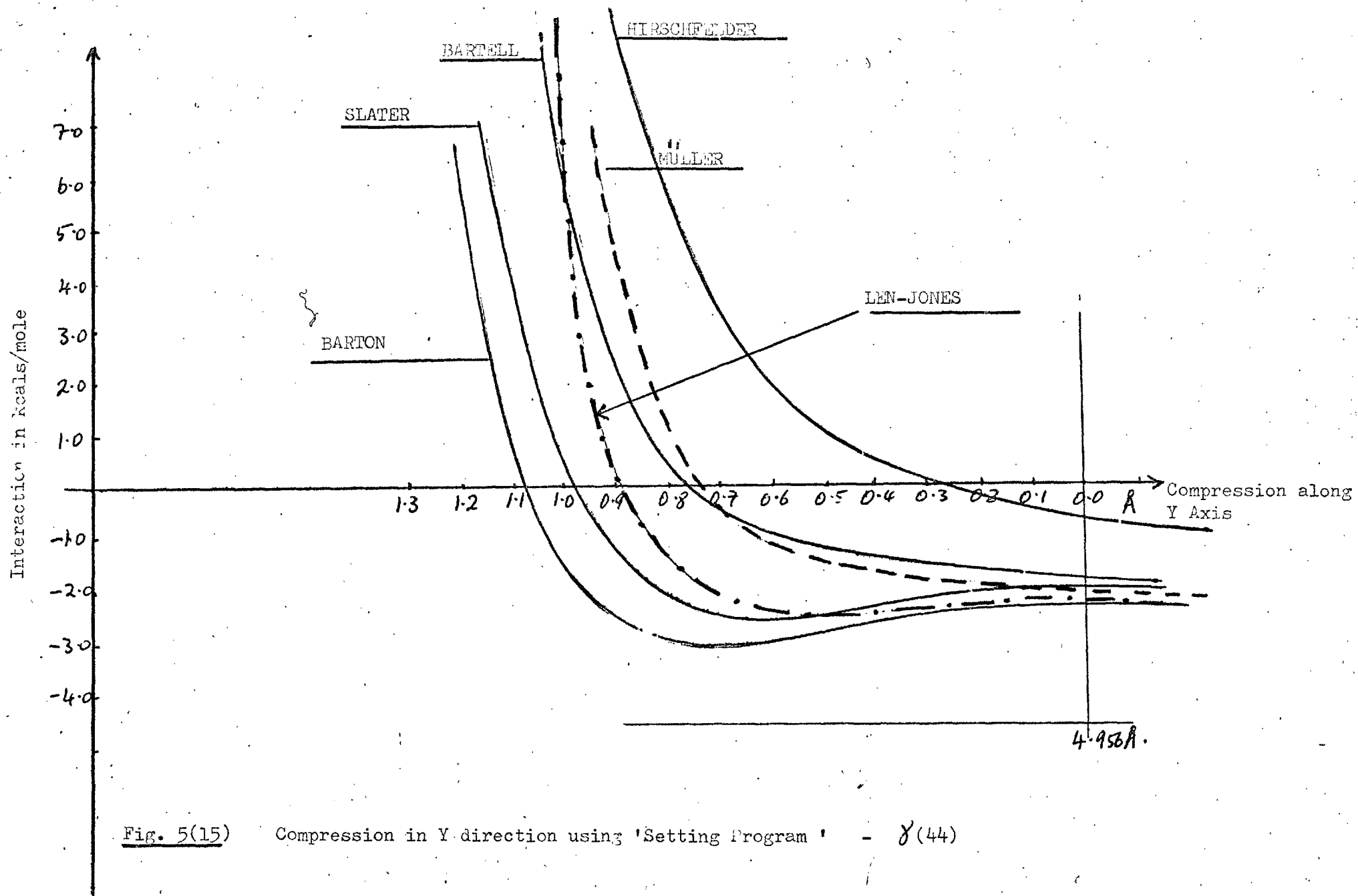


Fig. 5(15) Compression in Y direction using 'Setting Program' - $\gamma(44)$

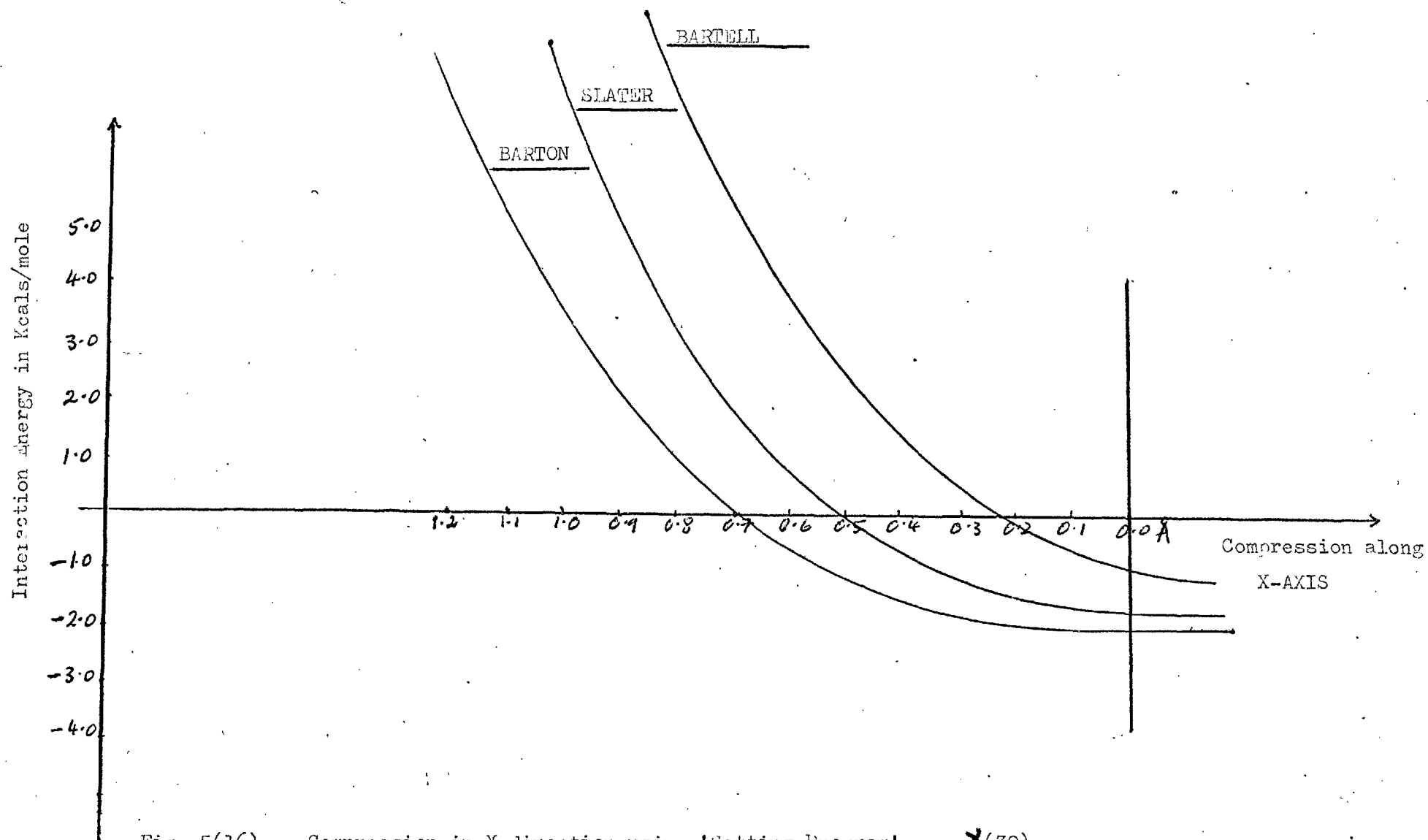


Fig. 5(16) Compression in X direction using 'Setting Program' - $\delta(30)$

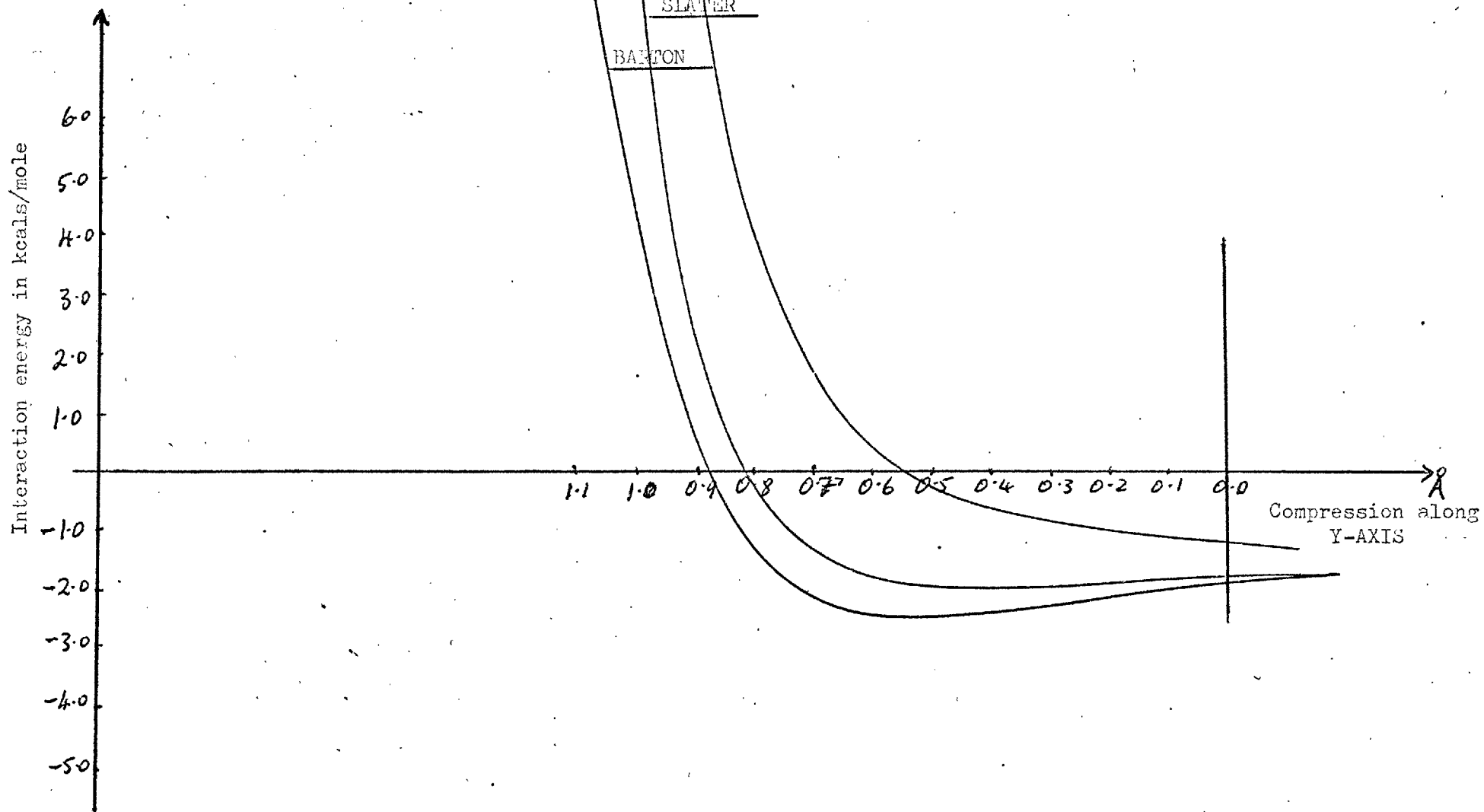


Fig. 5(17) Compression in Y direction using 'Setting Program' - 8 (30)

REFERENCES

- (1) Cameron A - ASLE Translation Vol 2; No. 2 (reprint)
- (2) van Battum CM and Broeder JJ - see Chapter(1) - reference (18)
- (3) Müller A Proc. Roy. Soc. 178 A 1941 (227)
- (4) Smith AE J Chem Phys 21 (1953) 2229
- (5) Akhmatov AS p 116
- (6) Akhmatov AS p 110

CHAPTER 6 - COMPRESSIBILITIES

6.1 The Importance of Compressibility Data

If Compression is assumed to be elastic a parabolic relationship can be shown to exist between the compressive *potential* and the compressive strain. If the forces are assumed to be additive the same laws should apply to solids i.e. upon compression repulsive forces should dominate and under tension the attractive predominate.

Using the last idea a check can be made on the suitability of the potential used in the programs.

The figures 6(1) and 6(2) show the data obtained for all repulsive potentials used, firstly combined with attractive point centres then with Scattering centres. It can be seen that in general the former shapes do not fit the boundary conditions whereas the latter do. This narrows down the use of potentials.

The other extremely important use is to test the theory of Boundary lubrication as put forward by van Battum and Broeder (1). The idea is to consider the work of friction as the sum of two parts, one of which is lifting the load to an equivalent compressive state. To test the theory, compressive data is required at points throughout the unit cell.

6.2 Theory of elastic compression

By assuming that a situation analogous to Hooke's Law exists between the compressive deformation and external pressure, relationships connecting all parameters of energy in boundary layers can be derived.

i.e. assuming

$$\Delta\epsilon = \frac{\Delta l}{l_0} = \frac{-1}{E_b} \phi \quad \text{--- (1)}$$

Where $\Delta\epsilon$ = compressive strain
 Δl = change of distance; $(l - l_0)$
 l_0 = equilibrium distance
 E_b = Elasticity modulus of compression
 ϕ = external pressure

$$\therefore \frac{l - l_0}{l_0} = \frac{-1}{E_b} \phi$$

Using $\phi = -\frac{\partial \epsilon}{\partial l}$ i.e. Force is the negative gradient at any point on an energy distance graph

$$\therefore \frac{l - l_0}{l_0} = \frac{1}{E_b} \frac{\partial \epsilon}{\partial l}$$

Consider Compression from l_0 to l and the interaction energy to be ϕ_0 and ϕ at these points.

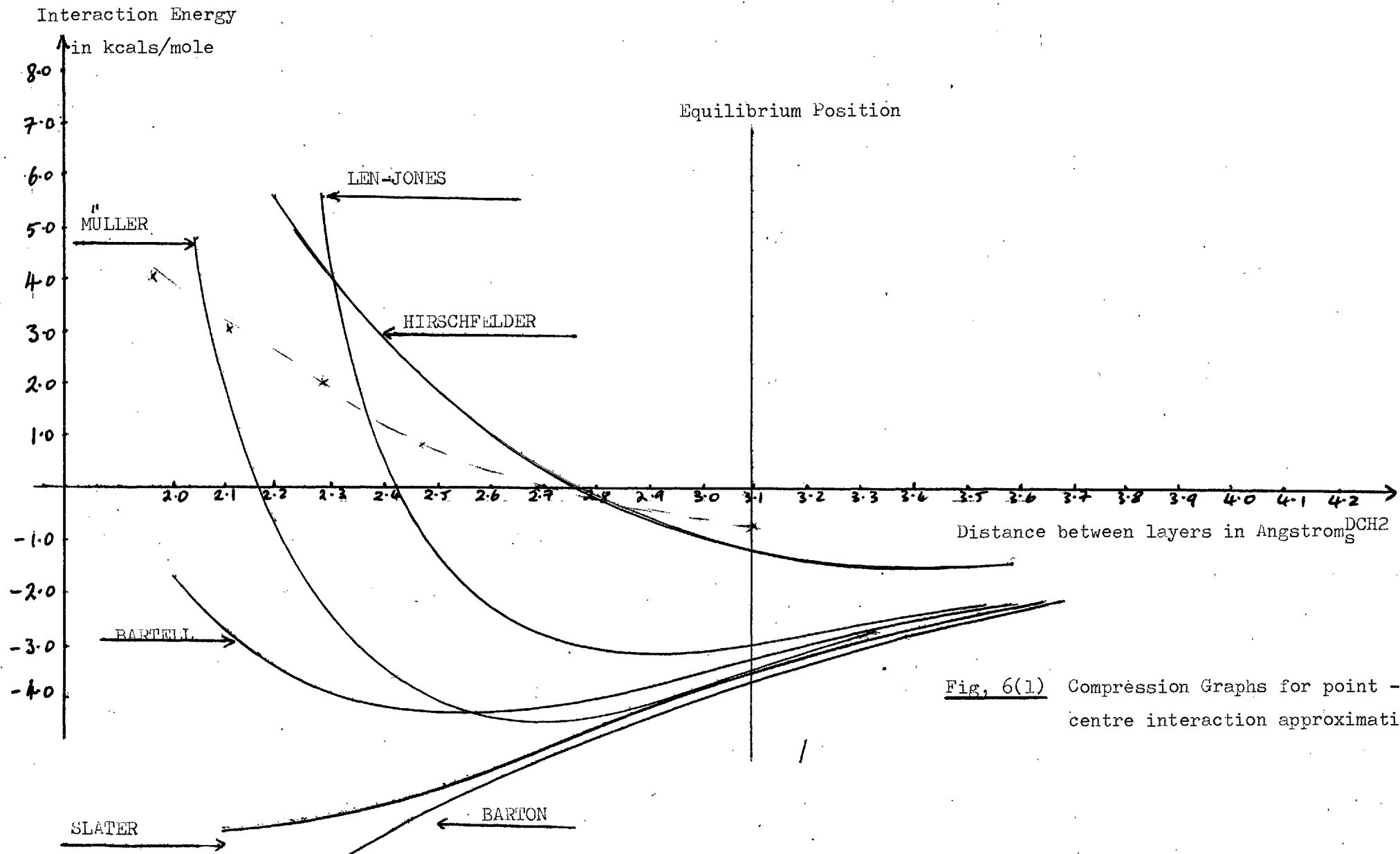


Fig. 6(1) Compression Graphs for point -
centre interaction approximations

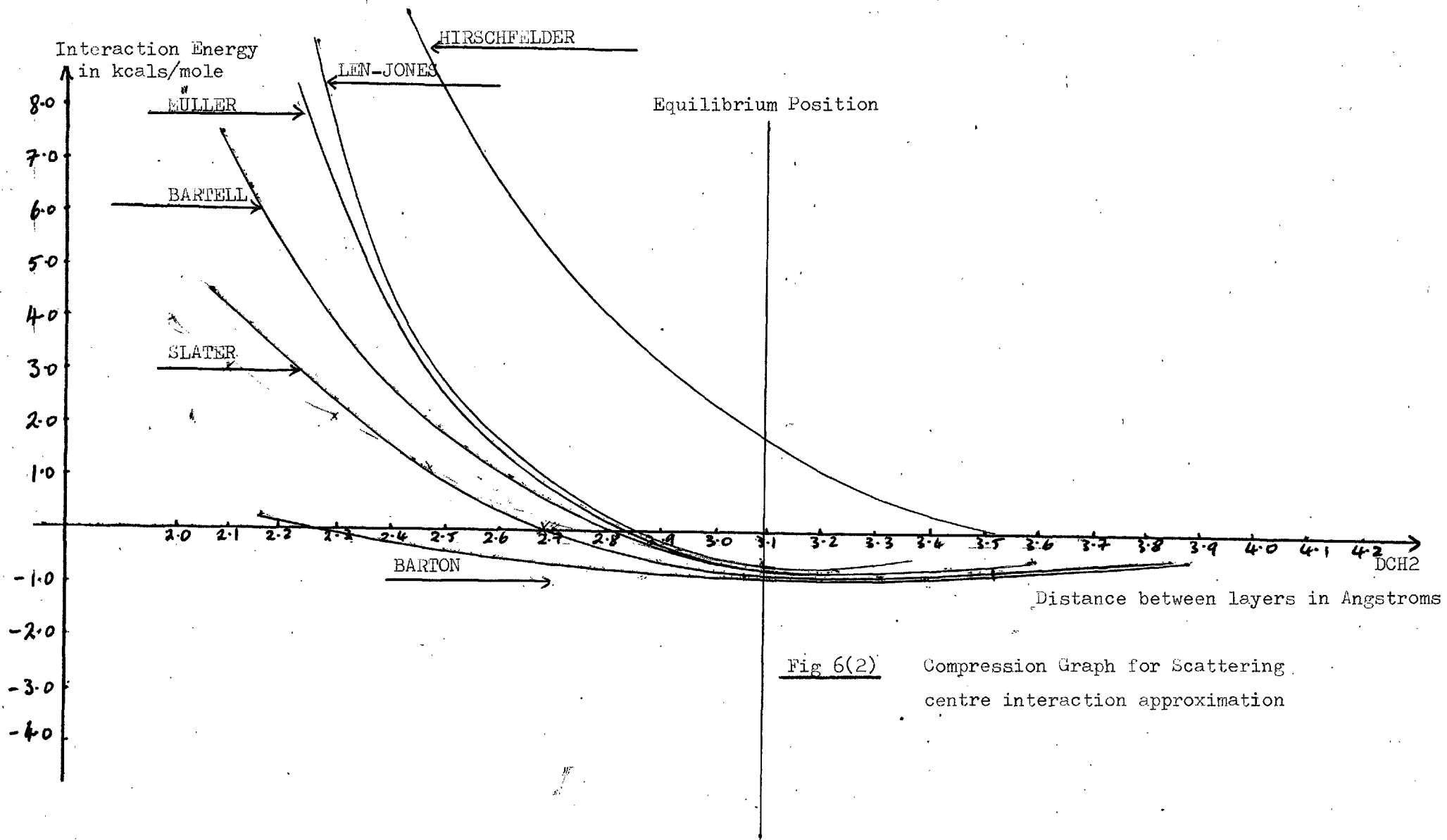


Fig 6(2)

Compression Graph for Scattering
centre interaction approximation

By integrating

$$\frac{l_0}{E_b} \int_{\phi_0}^{\phi} d\phi = \int_{l_0}^l (l - l_0) dl$$

$$\therefore \frac{l_0}{E_b} (\phi - \phi_0) = \frac{(l^2 - l_0^2)}{2}$$

$$\therefore \frac{l_0}{E_b} (\phi - \phi_0) = \frac{1}{2} (l - l_0)^2 \quad \text{--- (2)}$$

And by using equation (1) it follows by introducing A the area of cross section of the chain to give energy / CHAIN

$$(a) \quad \underline{\phi = f(\phi)} \quad (\phi - \phi_0) = \frac{A l_0}{2 E_b} \phi^2 \quad \text{--- (3)}$$

$$(b) \quad \text{and } \underline{\phi = f(\phi, l)} \quad (\phi - \phi_0) = \frac{1}{2} \phi (l - l_0) \quad \text{--- (4)}$$

It can be seen that graphs of interaction energy /chain against distance compressed, using the given assumption will be parabolas. ϕ_0 will differ (energy at equilibrium) for each type of potential and a sliding parabolic curve on some perspex was adapted to test the potentials, and it was found that most of Fig 6(2) potentials fitted very well. As l_0 and A, is the same for each case the only factor contributing to the different gradients will be the Elasticity E_b .

6.3 Applicability to Boundary Layers

In relation to XY compression in Chapter 5, Müller stated that compression in the Z plane is an order of magnitude higher than in the XY directions. He attributed this to the stronger co-valent bonding in the Z direction as opposed to the weaker polarisation forces in the XY direction. A monolayer under an external pressure will experience a resistance to the mutual approach of the CH_3 end groups and a resistance to the mutual approach of the CH_2 groups. The latter are opposed by valencey forces and would not substantially alter the potential profile when the model is sheared. In the literature it is always assumed that the approach of the CH_3 groups to be equal to the modulus of the chain i.e. Akhmatov (2), although Cameron (3) assumed the CH_3 mutual approach to be equal to the XY moduli.

6.4 Relationship between layer number, Elasticity and Compression diagram

It is an interesting fact that the yield strength of saturated fatty acids in boundary layers decreases with increasing layer thickness, Akhmatov (4). This property of anisotropy as a function of the number of monolayers extends to Compression diagrams and although reliable data is

scarce, Panova (5) managed to determine some compression diagrams for stearic acid.

Using this diagram as a guide, with the concept of infinite and finite layers (see Appendix B) and using known constants of layers. (7), (8), (9), the following Elasticity constants were calculated as a function of layer height.

- (a) 100 molecular layers.
 $E_I = 700 \text{ Kg/cm}^2$ $E_F \approx 0.5 \text{ kg/cm}^2 \quad \times 1400$
- (b) 50 molecular layers
 $E_I = 1.71 \times 10^3 \text{ kg/cm}^2$ $E_F = 2.43 \text{ kg/cm}^2$
- (c) 25 molecular layers
 $E_I = 5.74 \times 10^3 \text{ kg/cm}^2$ $E_F = 8.2 \text{ kg/cm}^2 \quad \times 700$
- (d) 20 molecular layers
 $E_I = 7.35 \times 10^3 \text{ kg/cm}^2$ $E_F = 10.5 \text{ kg/cm}^2 \quad \times 700$
- (e) 1 molecular layer
 $E_I = 10^{10} \text{ kg/cm}^2$ $E_F = 3.47 \times 10^6 \text{ kg/cm}^2 \quad \sim \times 300$

where E_I = represents infinite layers and E_F finite layers

These were plotted on log-linear paper and presented in fig. 6(3).

Also using this diagram and equation (2), fig. 6(4) was plotted which represents the interaction energy curve against DCH₂ (the layer distance) at zero displacement as a function of Elasticity. This only gives a trend, as stressed in the first Chapter, as Panova's anisotropic compressibilities most certainly involve unknown structural changes of fatty acids under pressure.

6.5. Anisotropic Compression of Layers.

Because the probable structural changes in compression are unknown the model must cope with the anisotropy within its parameters i.e. the mutual approach of CH₃ groups. If the information in fig 6(3) is plotted on a log-log scale, fig. 6(5), various conclusions can be drawn. A continuous distribution of gradients ranging from approximately - 1.5 to - 4.5, or any number of breaks in straight line gradients representing structural changes i.e. -2 to -3. Akhmatov quotes (6) an inverse law between layer thickness and yield strength which implies shear across the slip plane. Thus it seems reasonable to apply an inverse proportion law governing CH₃ - CH₃ approach. Both an inverse

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The concepts of gradients of physical properties in the Z axis is associated with liquid crystals or quasi solids. Fuks and Akhmatov provide experimental evidence for such films differing from bulk properties i.e. mechanical and elastic constants. Hardy attributes the anomalous nature to the influence of the field of the solid phases and other authors to structural changes caused indirectly by the solid. A theory of elasticity varying as layer height for long chain molecules is given by Frenkel - a full survey is given in references (4), (5), (6) and (7).

Another example of the program approaching a real situation is considered in Appendix B. The concept of 'infinite layers' is an ideal situation where no lateral expansion can occur under compression so the elasticity is greater than for 'finite layers'. Reference (6) shows that the two elasticities can be related by $E'_{(INF)} = \gamma E_{(FIN)}$ where γ is a 'steric factor' due to the resistance to an increase in cross section and is a function of Poisson's ratio. For normal solids Poisson's ratio is in the range 0.25 to 0.33 and in experiments Panova shows that for boundary layers of stearic acid it is 0.499 i.e. approaching 0.5, a limiting state. References (5) and (6) gives information of the elastic constants of stearic acid as a function of layer height i.e. knowing E (FINITE) is 0.25 kg/cm^2 for 100 monolayers and $3.47 \times 10^6 \text{ kg/cm}^2$ for a monolayer and using the slopes from experimental curves elasticity constants can be calculated. As Poisson's Ratio is known, infinite layers are also considered for interests sake - using $E' = \gamma E$. These relationships were plotted on fig. 6(3) and 6(5). (The value of γ is approximately 700 on the graphs.)

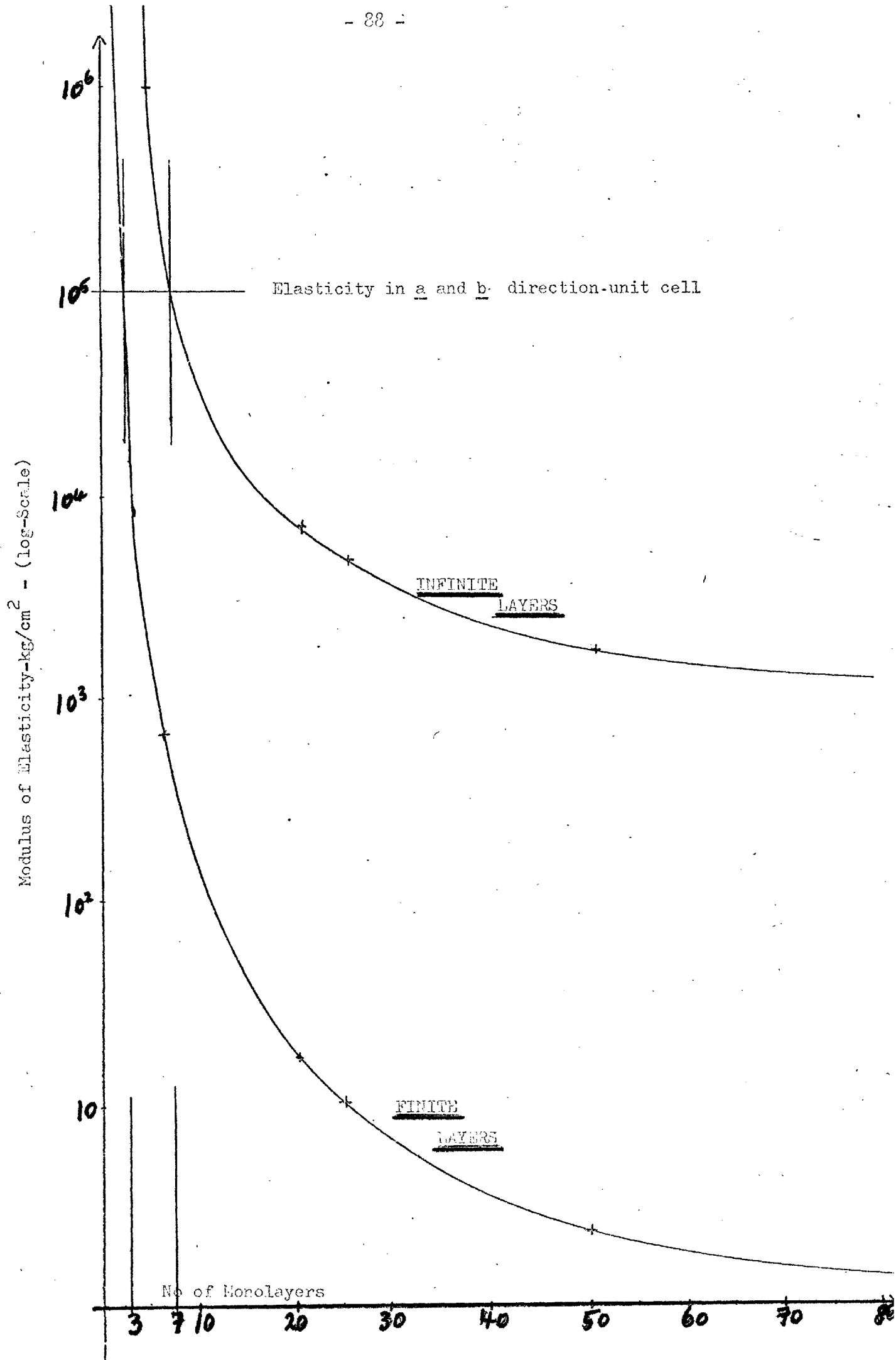


Fig. 6(3) Graph of Elastic constants against number of monolayers.

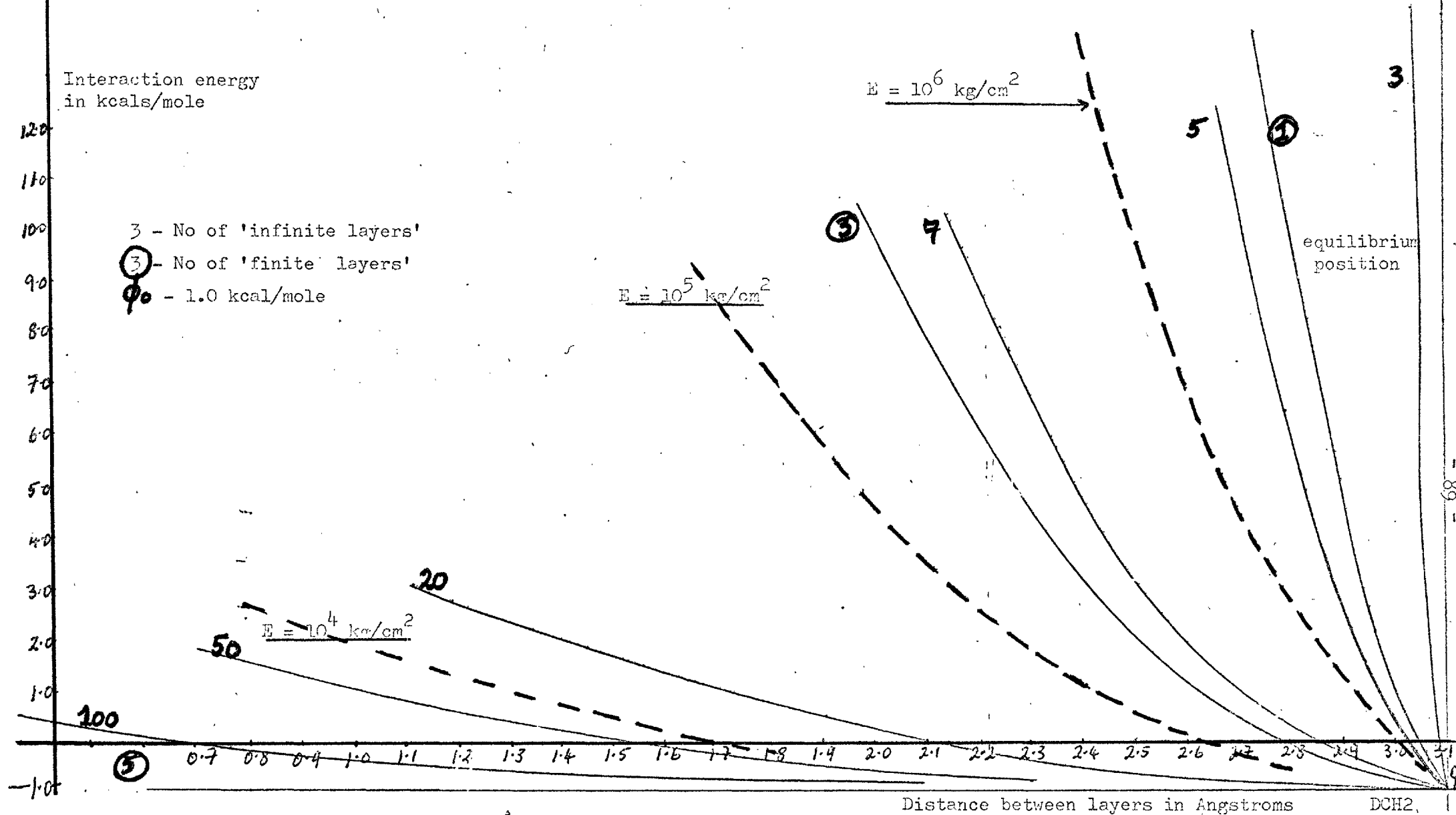


Fig. 6(4) Compression Graph of Fatty Acids as a function of layer height and Elasticity.

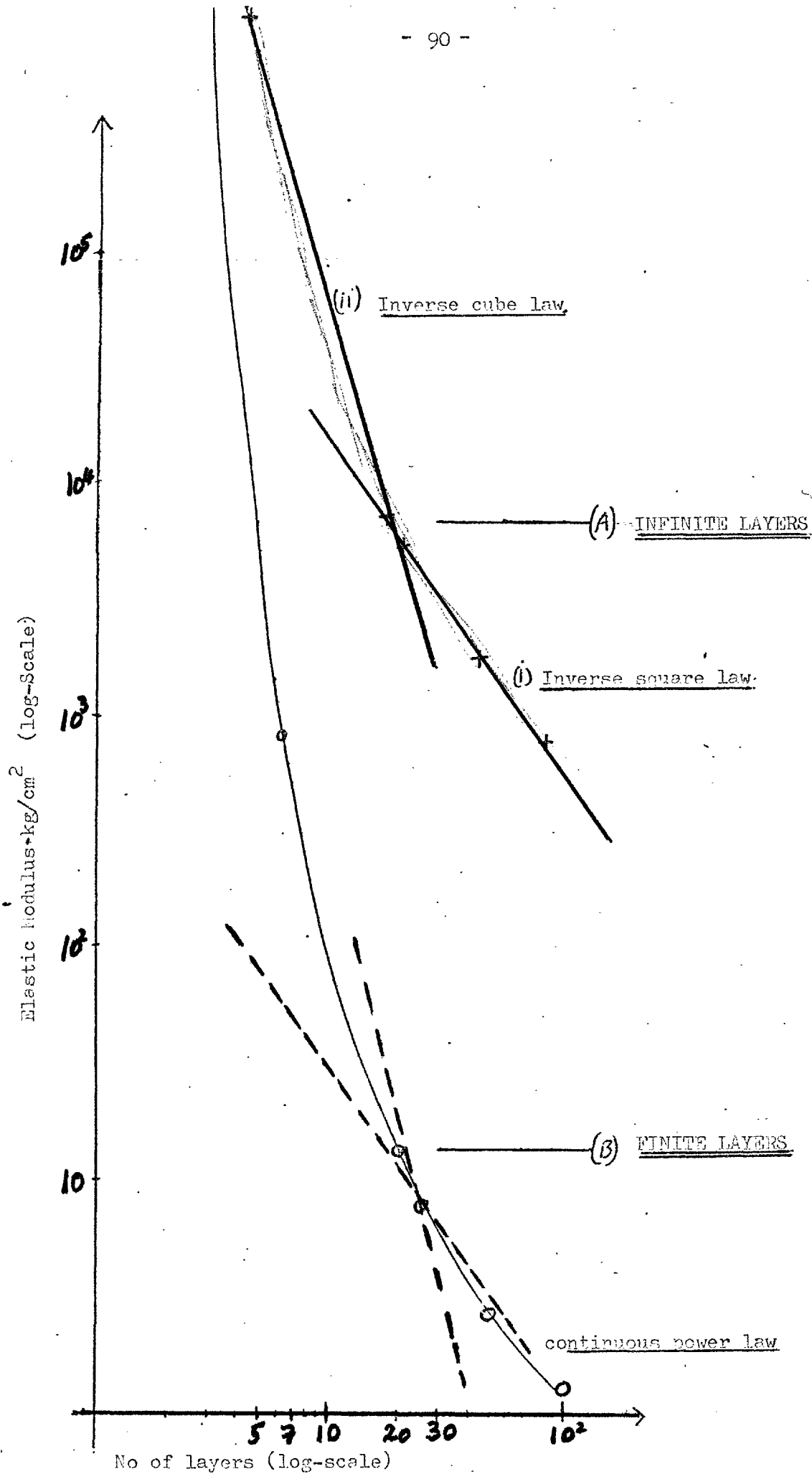


Fig. 6(5) Graph of Elastic constants against number of layers (log-log)

and inverse square law were investigated i.e. - fig. 6 (6) which represents distributions from 1 - 100 monolayers expressed in a weighting system from 1.0 to 0.0. The first layer is given the arbitrary value of unity the second 0.5, the third, fourth and fifth layers 0.25 etc. Thus if the total amount of $\text{CH}_3 - \text{CH}_3$ gap closure is known, the gap decrease across the slip plane can be calculated using the weighting system. Any excessive decrease across the first few gaps is assumed to be taken up by the covalent bonds of the chain. Akhmatov assumes the chains will form a mesh structure but as shown in Appendix II this is unreasonable using this particular model.

6.6 Correlation of no of layers with potential functions.

The problem remains to link figs 6(2) and 6(4), the actual potential profiles obtained and the theoretical potential profiles expressed in terms of the number of layers and their Elastic constants.

The method described in (6.5) was used to gauge the gap distance between the methyl groups in the symmetry plane midway between the two solid surfaces for 101 layers, 51, 21, 7, 5, 3 and a monolayer. An example using 7 layers will illustrate the method.

N.B. Every suitable potential used with respect to Compression diagrams can thus be used to represent the properties of a slip plane under compression. Differing layer thicknesses will be representent by a different potential.

Example using 7 layers

The term 7 layers is taken to mean 7 dimers, thus implying 7 methyl gaps with slip taken place across the weakest gap, (the symmetry plane), in this case the 4th Gap.

$$l_0 = 3.09 \text{ \AA}$$

The Infinite Elastic Modulus of 7 layers = 10^5 kg/cm^2 from fig 6(3)
Using $l_0 = 3.09 \times 7 = 21.63 \text{ \AA}$

Consider equation (1) and an external pressure of 10^4 kg/cm^2

$$\therefore \Delta l = 0.1 l_0 = 2.163 \text{ \AA}$$

$$\therefore \Delta l (\text{Half profile}) = 1.0815 \text{ \AA}$$

Assuming anisotropic compression - shear at 4th gap. and using fig. 6(5) with Δd as the smallest increment.

$$4 \Delta d + 2 \Delta d + \frac{4}{3} \Delta d + \Delta d = 1.0815$$

(See 6.7)

$$\therefore \underline{\Delta d = 0.13 \text{ \AA}}$$

To find representation Modulus using equation (1)

$$l_0 = 3.09 \text{ \AA} ; \text{ Pressure} = 10^4 \text{ kg/cm}^2$$

$$E_7 = \frac{10^4 \times 3.09 \times 10}{1.13} = \underline{2.37 \times 10^5 \text{ kg/cm}^2}$$

Using $\Delta d = 0.13 \text{ \AA}$ and the external pressure 10^4 kg/cm^2 it can be seen that

assuming elastic compressions the pressure needed to compress the system by $0.1 \text{ \AA}$ is equal to $7.7 \times 10^3 \text{ kg/cm}^2$. Thus a Lennard-Jones potential can be used to represent the properties of the slip plane of 7 layers.

6.7 Representation of Potentials

By comparing figs. 6(2) and 6(4) and using the calculations and arguments presented in section 6.6 the following results are presented.

f (1/d)			f (1/d ²)	
POTENTIAL	No of layers	p(0.1 Å)	Layers M	p(0.1 Å)
BARTON	(a) (50 - 100) M	1.167×10^2		
	(b) 5M	8.5×10		
HEN-BAR	(a) (50 - 100)M	1.167×10^2		
	(b) 5M	8.5×10	(7 - 5)M	2.55×10^2
SLATER	(a) 11M	3.0×10^3	100M	5.0×10^3
	(b) (3 - 5)M	$(2.1 \times 10^3 - 8.5 \times 10^3)$	3M	4.2×10^3
BARTELL	(a) 11M	3.0×10^3	20M	7.5×10^3
	(b) 3M	2.1×10^3	3M	4.2×10^3
MULLER	(a) 9M	4.5×10^3	20M	7.5×10^3
	(b) 3M	7.1×10^3	3M	4.2×10^3
LEN-JONES	(a) (7 - 9) M	4.0×10^3		
	(b) 3M	2.1×10^3		

Key p(0.1 Å) — pressure (kg/cm²) to compress layer by 0.1 Å
M — No of layers
(a) — Infinite layers
(b) — Finite layers

In some cases approximations have to be made. It can be seen that monolayers cannot be described i.e. the case when the representation parameters coincide with the actual pressures. Harder potentials had to be used to describe monolayers.

6.8 New potentials to describe monolayers.

For finite layers the elasticity is $3.47 \times 10^6 \text{ kg/cm}^2$, fig. 6(4). The typical repulsive potentials $A r^{-12}$ and $B \exp(-CR)$ were altered (because for steeper interaction curves the repulsive contribution has to be harder)

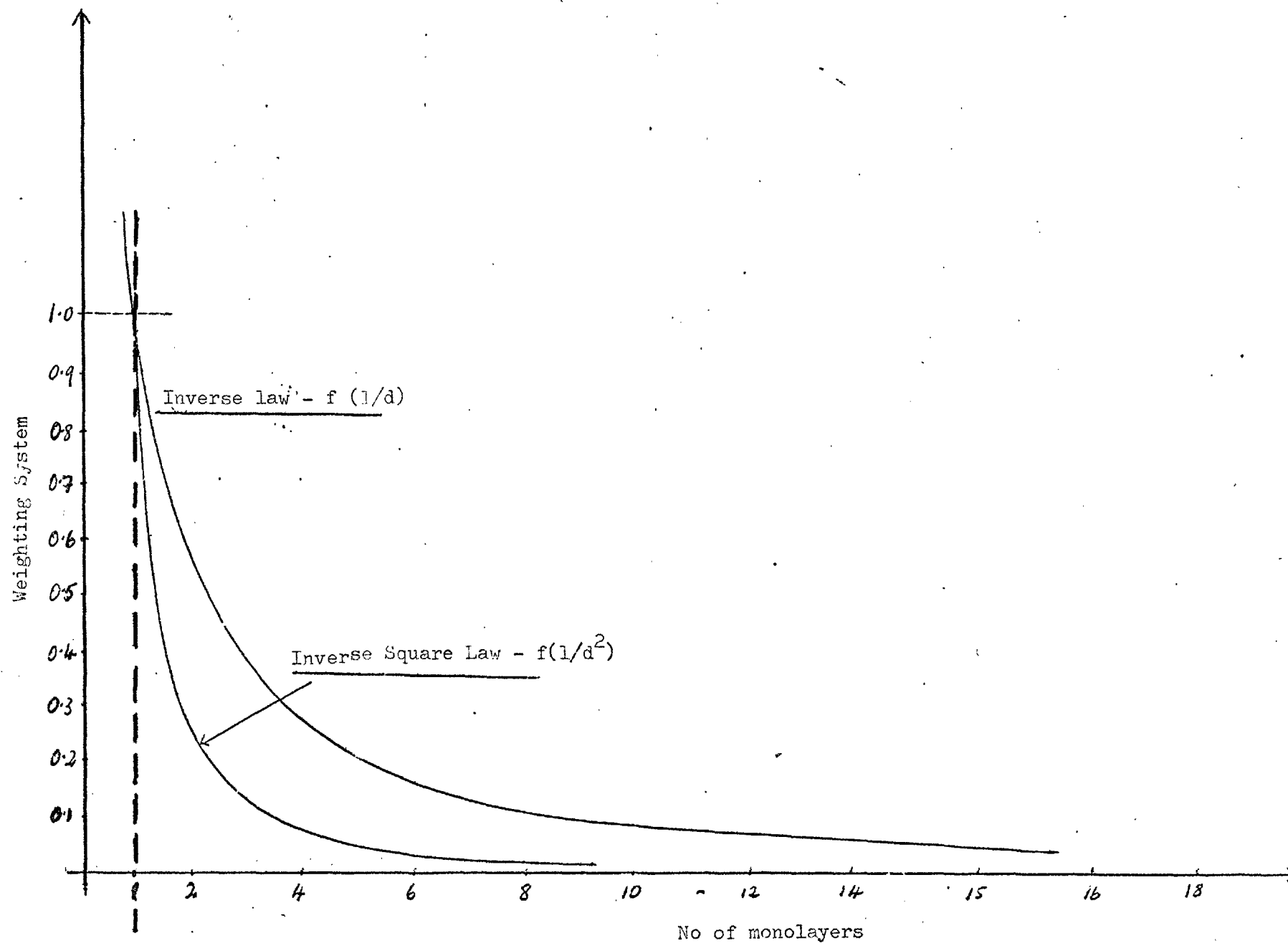


Fig. 6(6) - Monolayers expressed in terms of anisotropic distributions.

by increasing the constants A and B and decreasing C, it is found that although the resultant interaction profiles are harder they no longer have an equilibrium position at DCH2 equal to 3.09 Å.

To remedy this a completely new form of potential had to be developed using a Polynomial fit employing a Least Squares method. First a program was run compressing the system at equilibrium (D = 0.0) printing out all the H-H repulsion distances, their conversion to energy and the total repulsive potential. Comparisons were made of these parameters as a function of DCH2 and it was found that only one H-H bond was responsible for the majority of the total repulsion potential.

Using the plots of previous H-H potentials as a guide (see Chapter 3) new curves were drawn of H-H potentials. Fifteen points were plotted from 2.4 Å to 1.4 Å. These were fed into the computer as two arrays and a curve to the fourth power was obtained in terms of its coefficients.

i.e. $\phi(R) = C_0 + C_1 R + C_2 R^2 + C_3 R^3 + C_4 R^4$

The curve is a continuous fit and standard deviations of each point were also obtained to gauge the accuracy of the fit, in all cases five coefficients provided an adequate approximation. By introducing the X array as $\exp(-R)$ instead of R an exponential series can also be used.

i.e. $\phi(R) = C_0 + C_1 \exp(-R) + C_2 \exp(-2R) + \dots + C_n \exp(-nR)$

The potentials used to represent monolayers and multiples, depending on the infinite or finite approximation (a) 5M infinite and 1M finite fig. 7 (14)

$$\underline{C_n \exp(-nR)}$$

$$\begin{aligned} C_0 &= 23851.95 \\ C_1 &= -719840.62 \\ C_2 &= 8084480.755 \\ C_3 &= -40060570.308 \\ C_4 &= 73970856.86 \end{aligned}$$

(b) 3M infinite

$$\begin{aligned} C_0 &= 5416.1517 \\ C_1 &= -332542.67471 \\ C_2 &= 7637424.417 \\ C_3 &= -77765166.5508 \\ C_4 &= 2962203291.77 \end{aligned} \quad \text{fig. 7(13)}$$

N.B. The Len-Jones approximation fitted the two exponential functions exactly. These potentials were then checked for suitability and used in the programs - see Chapter 7, 8, and 9.

6.9 Introduction of ROCK and ROT

To introduce mobility into the compressive program the parameters ROCK and ROT can be used to alter the orientation of the H molecules in the methyl group. The compression at the origin was generally taken to be rigid and internal rotations introduced when a dynamic situation developed.

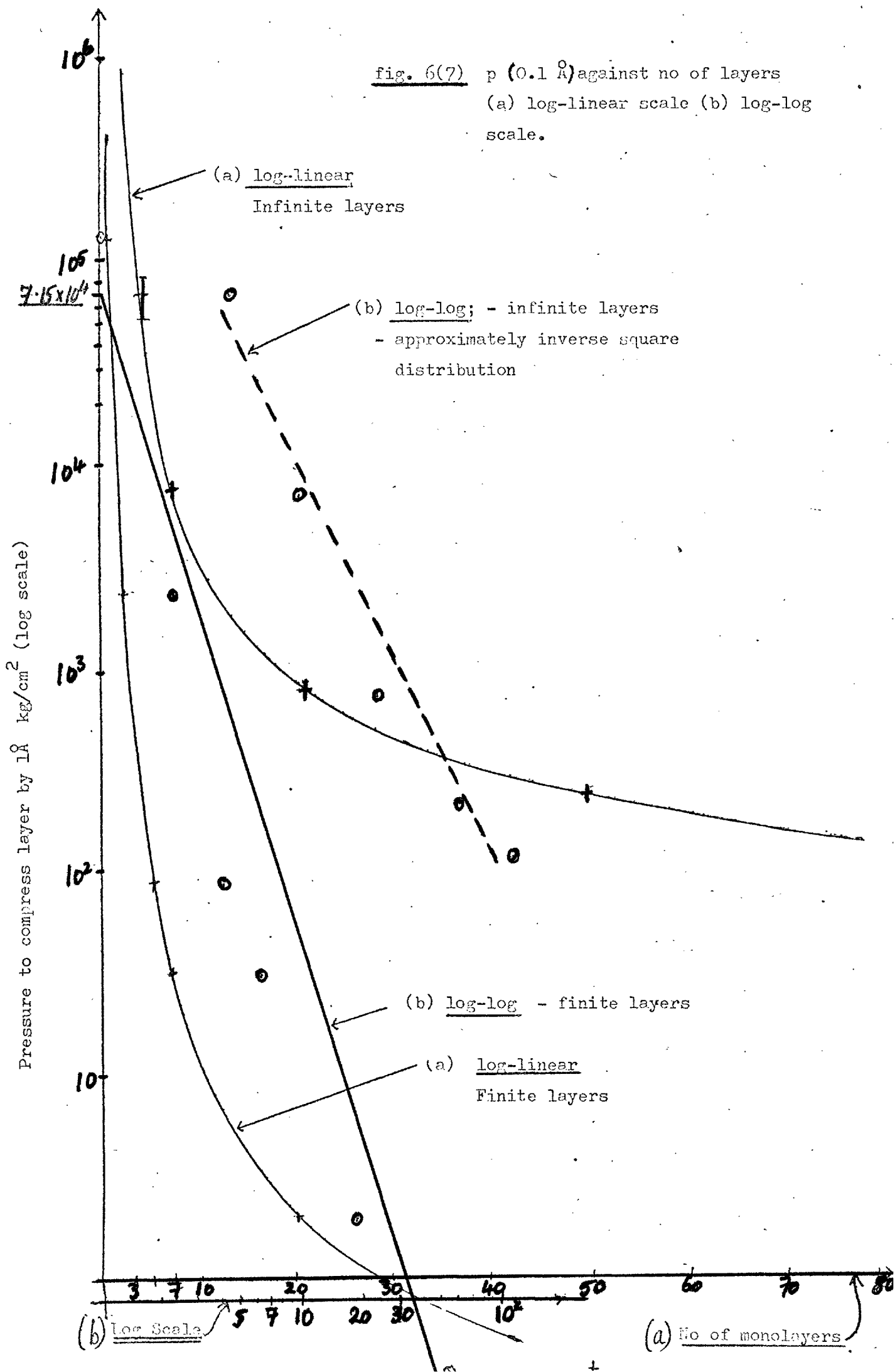
6.10 Conclusions

The very nature of compression implies the predominance of repulsive forces with respect to the attractive ones. Unfortunately in relation to monolayers and fatty acid layers in general, how these repulsive forces come into play is not known, whether it is predominately $\text{CH}_3 - \text{CH}_3$, $\text{CH}_2 - \text{CH}_2$ or structural changes or a combination of all three.

REFERENCES

- (1) Van Battum CM and Broeder JJ - see Chapter (1) - (18)
- (2) Akhmatov AS - p.266
- (3) Cameron AC - ASLE Transactions Vol 2; No 2
- (4) Akhmatov AS - p. 246
- (5) Panova - C.f. Akhmatov p. 255. - 264
- (6) Akhmatov AS - p.255
- (7) Akhmatov AS - p.262
- (8) Müller A - see Chapter (2) - (3)
- (9) Mizushima S - see Chapter (2) - (19)

fig. 6(7) p (0.1 Å) against no of layers
(a) log-linear scale (b) log-log scale.



CHAPTER 7 - SHEARING OF THE MODEL

7.1 Shear across the X-AXIS

In fig. 7(1) graphs are shown of shear across the X-AXIS as a function of the Setting Angle. The graph shows the effect of shearing the Barton - Point centre interaction curve at zero compression for setting angle of 30° , 50° , 55° , 65° , and 80° . It can be seen that for a rotation of 25° about 44° the potential barrier is reduced only by ≈ 1.5 kcal/mole. The situation is worse for scattering centre potentials and compressive states. i.e. the rotation of the molecules about their long axis has little or no effect (see Chapter 5).

7.2 Effect of Rotation of end groups

In fig 7(2) the same potential is shown under conditions of rotation and twisting of the methyl group (i.e. SET(44); zero compression; Barton-point centre energy; shear across the X-AXIS). Values of rotation of 0° , 10° , 15° , 20° , are shown, values of rock of 0° , 5° , 10° and 20° are shown and a combination (ROT/TILT), of 20/20 also included.

It can be seen that values of pure Rotation displace the maximum, but are not very effective; the values of tilt are very effective, combination values are not displaced very much and reduce the potential peak a considerable amount. It must be remembered that the work of rotating the end group must be considered part of the energy dissipated.

Programs were run to calculate values of the potentials used as a function of

(a) Distance - at 0.25 Angstroms in all directions.

(b) ROT/ROCK values of 0/0; 20/0, 0/5, 0/10, 0/20.

(c) For Cameron's loading system - i.e. 0, 40, 80, 120 ton/sq " representing gap distances (DCH2) of 3.09; 2.85, 2.65 and 2.45 Å. The gap compressability was taken as 10^5 kg/cm² which is the value in the a and b direction of the cell.

(d) For DCH2 values corresponding to 0, 40, 80, 120 ton/sq " assuming the axial compression to be that of a monolayer i.e. $E_c = 3.47 \times 10^6$ kg/cm². The potentials are treated with isotropic compression conditions.

(e) In the above case the potentials were also treated individually using the anisotropic compression functions.

7.3 Types of Friction

In the literature distinction is drawn between Static and Kinetic friction, **static** friction being the resistance force to start the system and kinetic being the resistance once the system is in motion.

Akhmatov (1) takes the kinetic friction to be the statistical result of breaking and forming bonds, having no counterpart in elastic theory.

By considering fig. 7(2) and relating the force of friction to X (i.e. Force = Energy/Distance) Static friction may be approximated to. From the diagrams $X \approx 1.3 \pm 0.1 \text{ \AA}$. But this does not provide a very satisfactory way of linking X-AXIS shear to shear in any direction, or describing Kinetic friction.

The parameters dependent on shear in the X-AXIS can be related to other directions by considering the periodic boundary condition of the cell. Fig 7(3). The X and Y axis are marked and the reproduction of the unit cell shown with the paths of periodicity i.e. across various diagonals of the cells. Programs were run partly as a check of the model and partly to gather potential profiles in comparison to the X-AXIS. It can be seen that the paths are not evenly distributed and only extend in an arc from $9^\circ - 76^\circ$, unless a vast number of programs are run to fill in the gaps.

A far simpler method is to consider the Energy dissipated/cm in any path and compare it to the energy/cm in the X-direction. The purpose being, that once X-AXIS parameters are known the statistical average will be a ratio to it.

7.4 Statistics of shear related to the X-AXIS

Using the results of potential as a function of distance inherent in fig. 7(3), equipotential diagrams of a unit cell can be drawn c.f. fig.7(4). This represents a Barton-Point centre interaction energy diagram as a function of θ (Angle of inclination), for zero compression. Six unit cells are shown and by considering the points A,B,C or D any displacement in any direction may be determined. By considering displacements in steps of 10° from 0° to 360° , of range $15 \text{ \AA}$ to $60 \text{ \AA}$, an increasingly smooth pattern of energy/cm compared to the X-AXIS value can be seen to occur - Figs.7(5), 7(6), 7(7), and 7(8). In all the diagrams the X-value is taken to be unity and all values as a $f(r, \theta)$ expressed in a ratio to unity.

It can be seen from the graphs that a Root Mean Square value can be calculated from the 36 individual values - or the average found by a square counting method (finding a circle of equal area). The area values for the figs are 0.69, 0.615; 0.64, 0.625 parts of the X-AXIS - which if a graph is drawn, is oscillating about the value 0.63 as the path distance increases.

Also from figs. 7(4-8) it can be seen that definite directions of least resistance to shear occur ; at the diagonals of the unit cells and the Y-axis. This will be discussed in Chapter 9 in relation to Physical and Chemical adsorption of the molecules. It may be noted that the greatest movement required by a single layer to attain a minimum is approximately 15° . (30° from the diagrams:- but the layers will both move as reaction forces are induced.)

The example quoted applies to zero load and a rigid system. As the load increases the origin potentials slightly alter and the equipotentials are more dense (a slightly larger area is used), but as the effect is predominately a repulsive one the profiles approximate to similar triangles which will not alter the ratio. A similar reasoning applies to the different repulsive potentials used. fig. 7(15). The ratios are altered when rotations of end groups are considered as the effect of dissipation of the rotational energy must be included in the ratio. Minimums still occur about the diagonals and the Y AXIS i.e. Average values for all exponential potential are expressed below as ratios to the X-AXIS.

Orientation	QUAD (A)	Y	QUAD (B)	rms
0/0	0.086	0.203	0.164	0.63
0/20	0.34	0.55	0.49	0.75

If a value of SHIFT (20) is considered (orientation of 20° to the vertical) a somewhat different picture emerges.

Orientation	QUAD (A)	Y	QUAD (B)
0/0	0.63	1.1	0.7
0/5	0.95	5.0	1.01

The significance of these results will be discussed in the next two Chapters.

7.5 Investigation of lifting with shearing

The idea of the force of friction being the sum of some shearing process plus the lifting of one layer over the other has been put forward by van Batsum & Broeder (See Chapter 1). This is just another version of Coulomb's theory of friction c.f. $\mu = \tan \theta$

i.e. Consider total energy dissipated be E - comprised of shearing force ΔE plus lifting force $N \times \Delta d$ (N equal to the load and distance raised Δd .)

$$E = \Delta E + N \cdot \Delta d$$

$$\text{Force} = \frac{E}{X} = \frac{\Delta E}{X} + \frac{N \cdot \Delta d}{X}$$

(converting energy to force over distance X)

$$\mu = F/N = \frac{\Delta E}{XN} + \frac{\Delta d}{X} \quad - (1)$$

The coefficient of friction should be the sum of the shearing process plus Coulomb's $\tan \theta$ contribution. It is interesting here to consider

Bikerman's theories (see Chapter 1) in relation to equation (1). The author maintains that the force of friction only exhibits itself against the external load - hence μ would be $(\Delta d/X)$ in equation (1).

$$\text{i.e. Force} = \frac{\Delta E}{X} + \mu N \quad - (2)$$

with a constant force F_0 added on, $(\Delta E/X)$

To investigate these concepts compressability curves must be determined at the maximum curve profile ($D = 2.4 \text{ \AA}$ on the X-AXIS). It was seen in Chapter 6 that only some potentials are appropriate for the model. The compressability curves of these potentials for the X-AXIS case are shown in figures 7(9), 7(10), 7(11), 7(12), 7(13), 7(14) as a function of ROT and ROCK. The loads can be calculated from the gradients of the curves - the difference between comparable gradients is ΔE and Δd can be read off the DCH2 axis. The last value must be halved as both layers are going to repel each other by action and reaction forces. X was taken so the energy dissipated / cm could be calculated. fig. 7(15).

7.6 Statistics of Lifting

Programs were run to determine compressabilities of the layers at several orientations and ranges - i.e. compressing at maximum potential profiles - fig. 7(4). It was found the Δd was approximately constant for individual potentials (proportional to μ) while ΔE differed as a function of orientation, tilt and rotation.

Typical results were as follows:

- (a) Compressing the molecules in quadrant A, range $6.5 \text{ \AA}$, orientation 34.15° to the X-AXIS and Rotation 0/20 will ensure results corresponding to a local potential maximum. The values of Δd remained consistent to the X-AXIS readings ($\pm 10\%$), inferring the coefficient of friction is approximately constant to X-AXIS values. (assuming the values of E do not alter drastically with load). Values of the decrease in the ΔE values compared to X-AXIS readings are Barton 55%; Bartell 35%; Muller 25%; Slater 35% and the monolayer potentials 25%. Average of 35% decrease i.e. 65% the value of the X-AXIS.
- (b) Compressing the molecules in quadrant B, range $6.5 \text{ \AA}$, orientation 145.85° to the X-AXIS and rotation 0/20. Again Δd values are consistent and the average ΔE value is 75% the value of the X-AXIS.
- (c) The remaining minimum direction is the Y-AXIS. Again similar results are obtained for 0/20 rotations.

In general the minimum values of ΔE are 60-80% of X values and μ remains approximately constant to the corresponding X -values.

REFERENCES

- (1) Akhmatov A.S. p 279

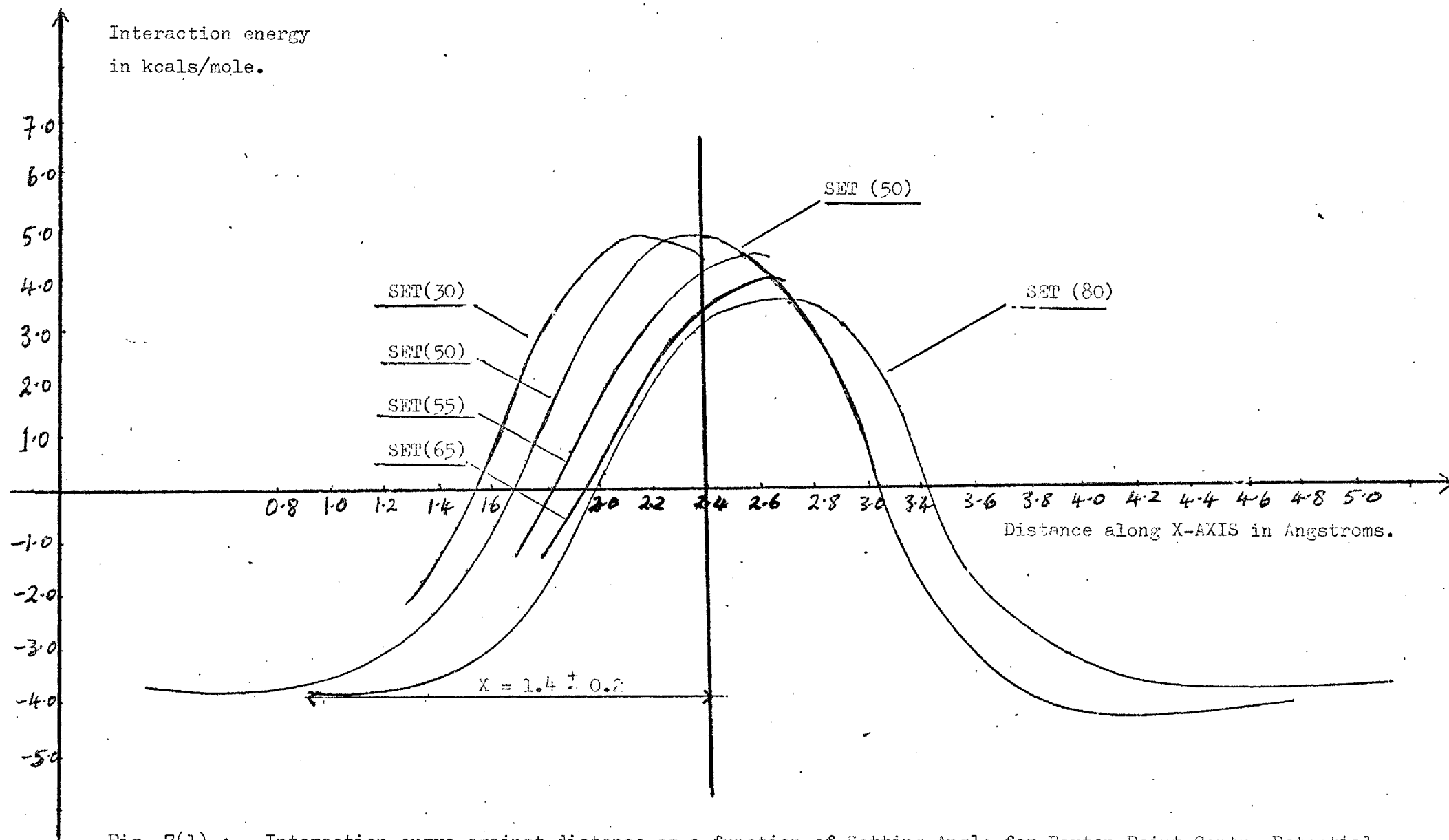


Fig. 7(1) :- Interaction curve against distance as a function of Setting Angle for Barton Point Centre Potential - zero compression.

Interaction Energy
in kcals/mole

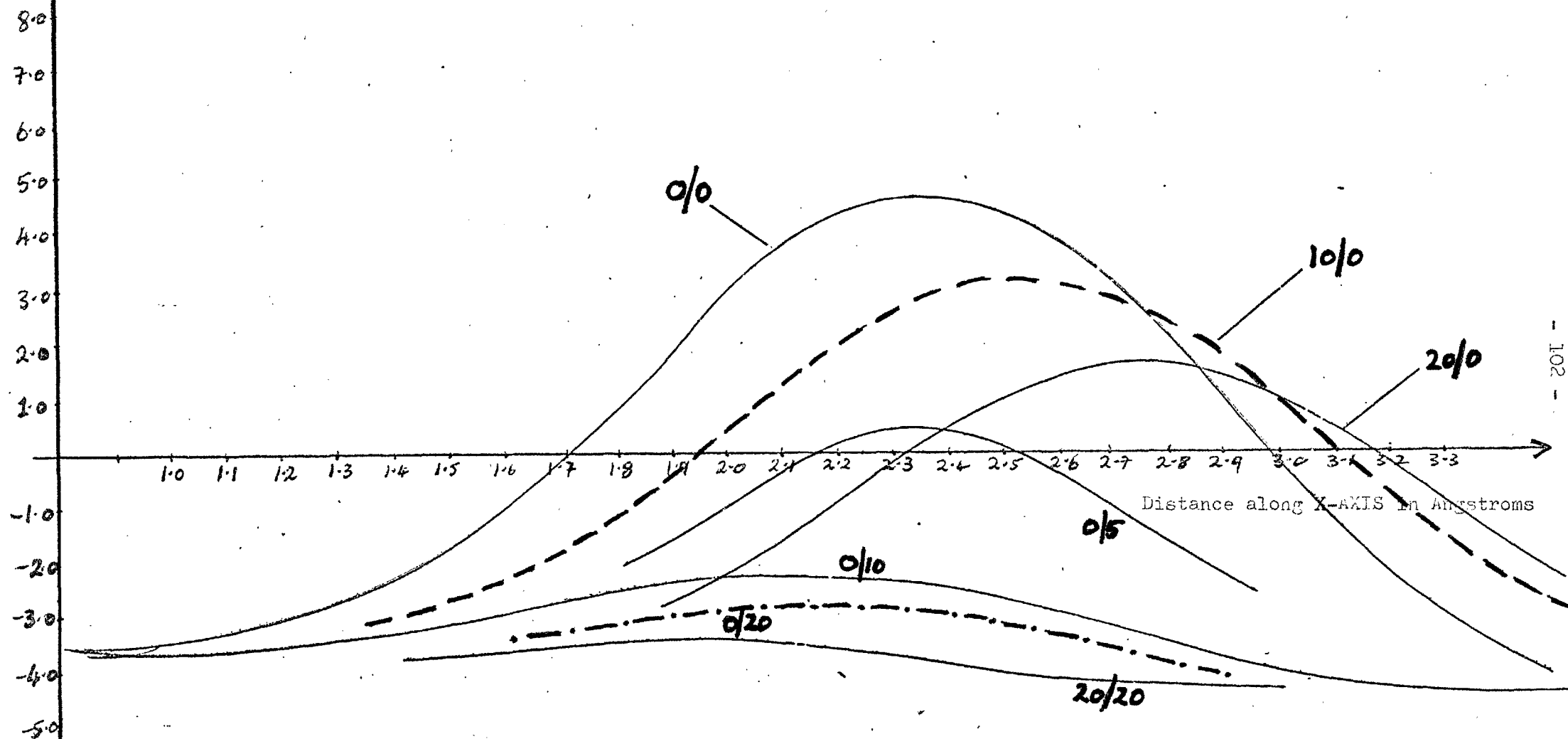


Fig. 7(2) :- Interaction Energy against distance as a function of RPT/ROCK ratio - for Barton Point Centre Potential - zero compression.

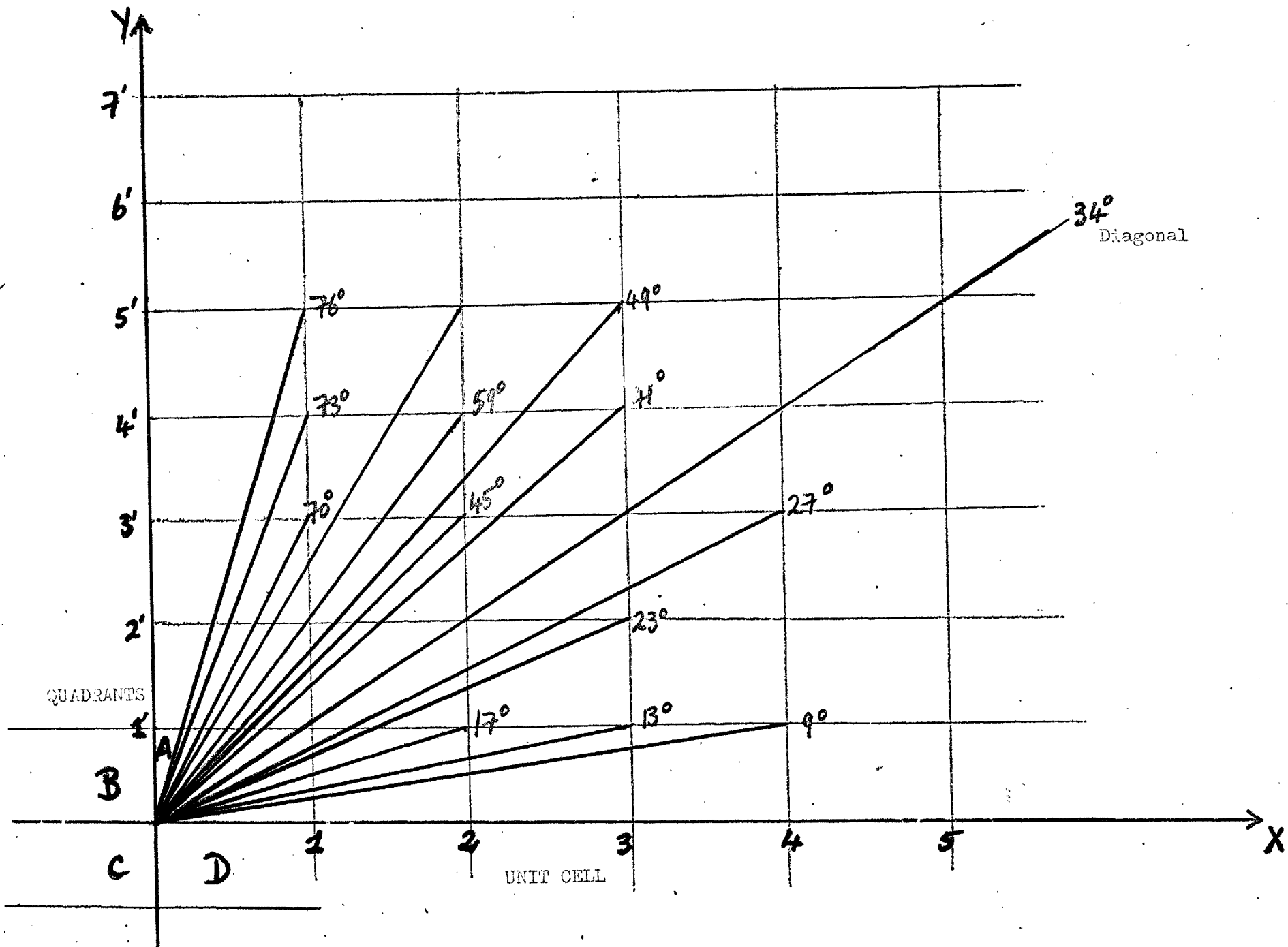


Fig. 7(3) :- Graphical description of paths from the origin as a function of periodicity, and angle of inclination to X-AXIS.

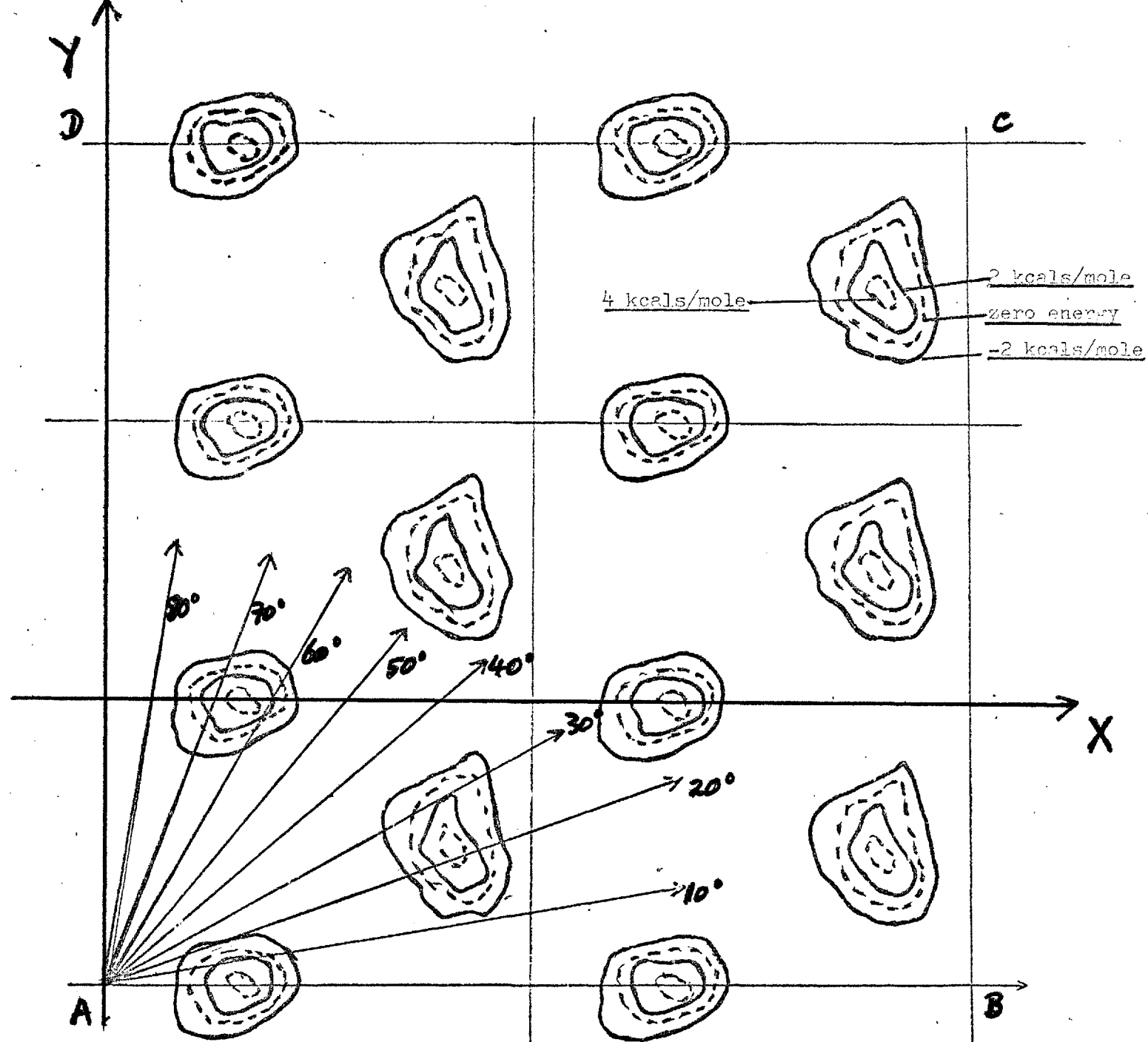


Fig. 7(4) :- Diagram of equipotentials for six unit cells with respect to Barton Point Centre. Potential when shearing the model in steps of 10 degrees.

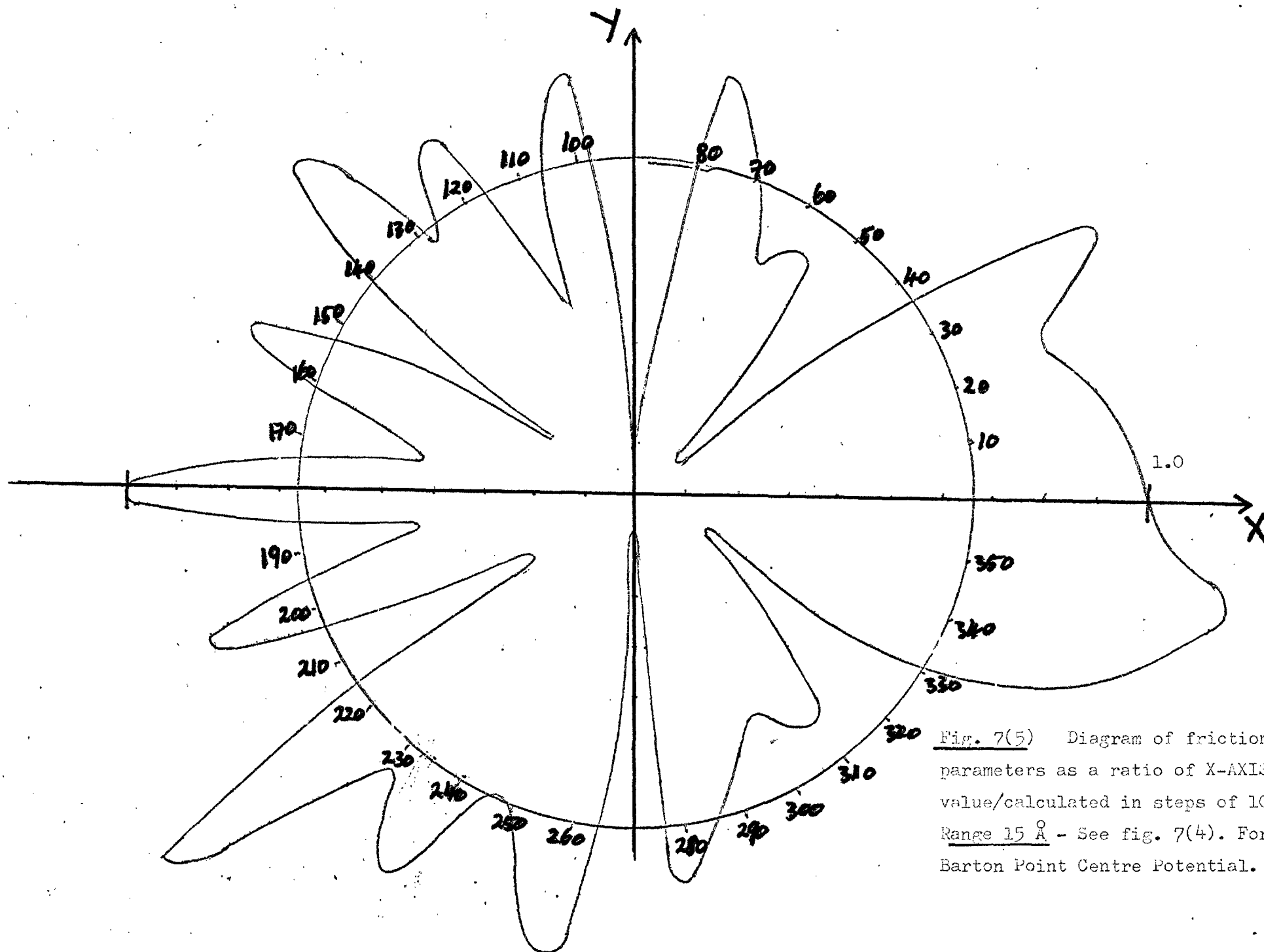


Fig. 7(5) Diagram of friction parameters as a ratio of X-AXIS value/calculated in steps of 10° - Range $15 \text{ \AA}$ - See fig. 7(4). For Barton Point Centre Potential.

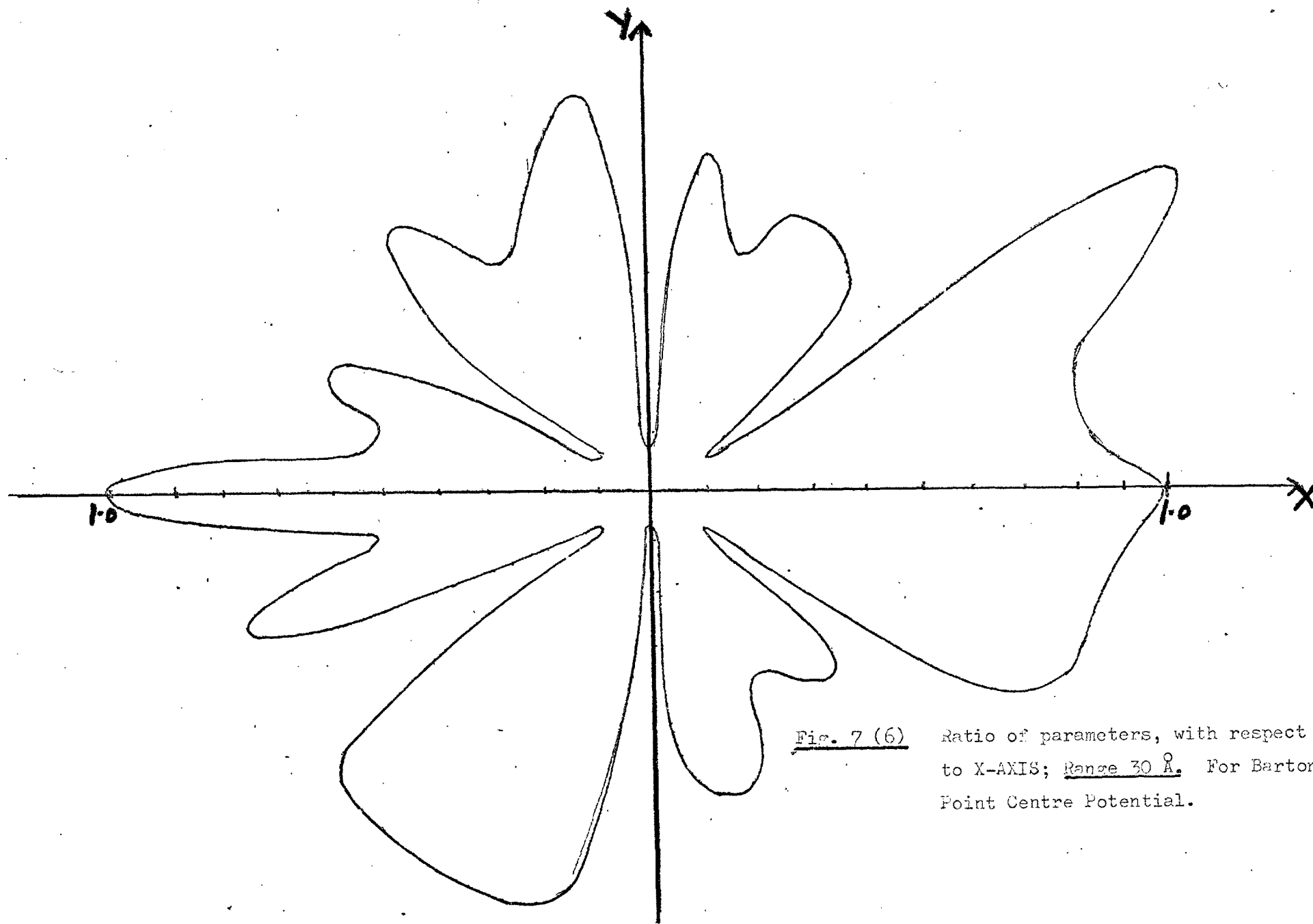


Fig. 7 (6) Ratio of parameters, with respect
to X-AXIS; Range 30 Å. For Barton
Point Centre Potential.

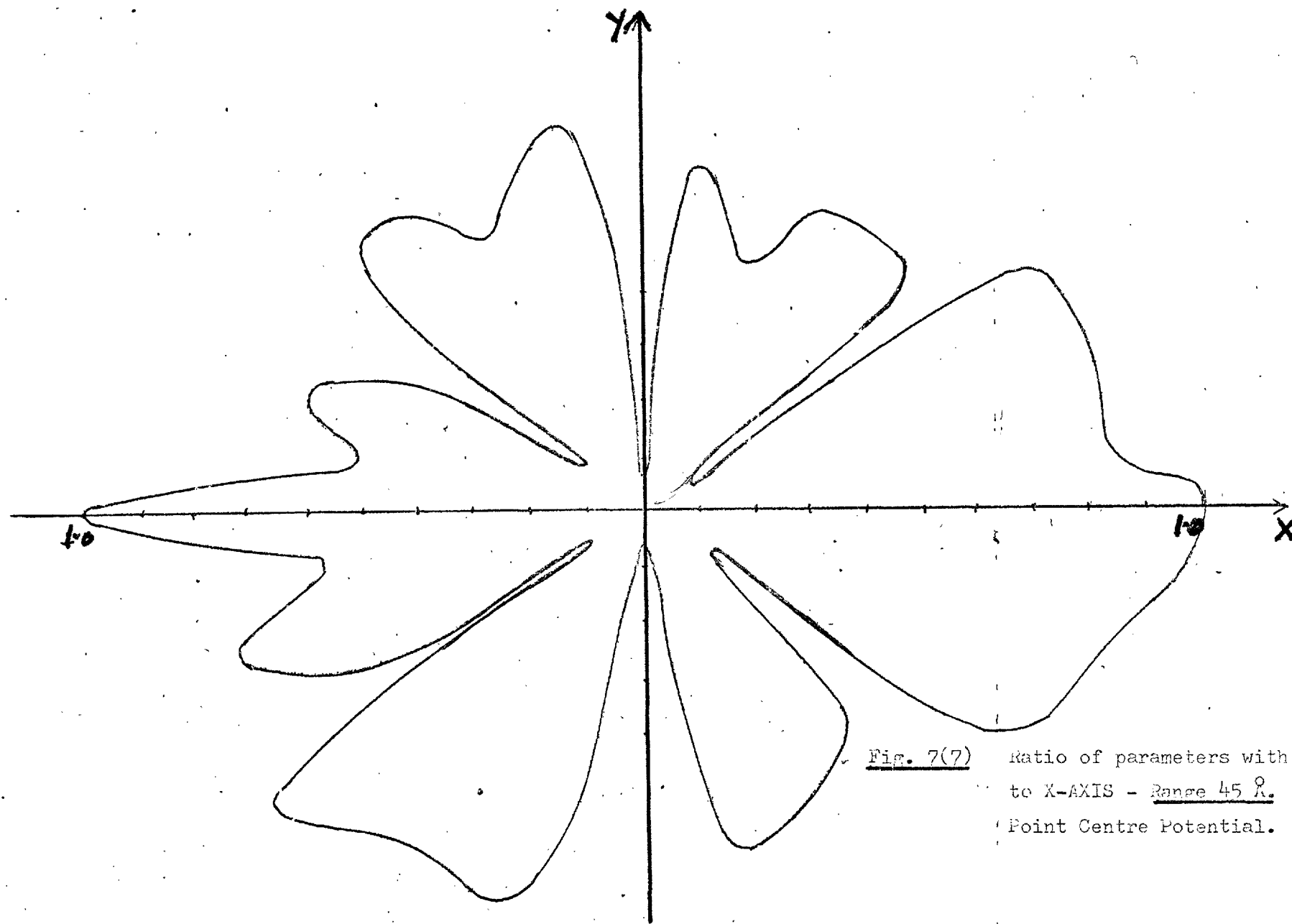


Fig. 7(7) Ratio of parameters with respect
to X-AXIS - Range 45 R. For Barton
Point Centre Potential.

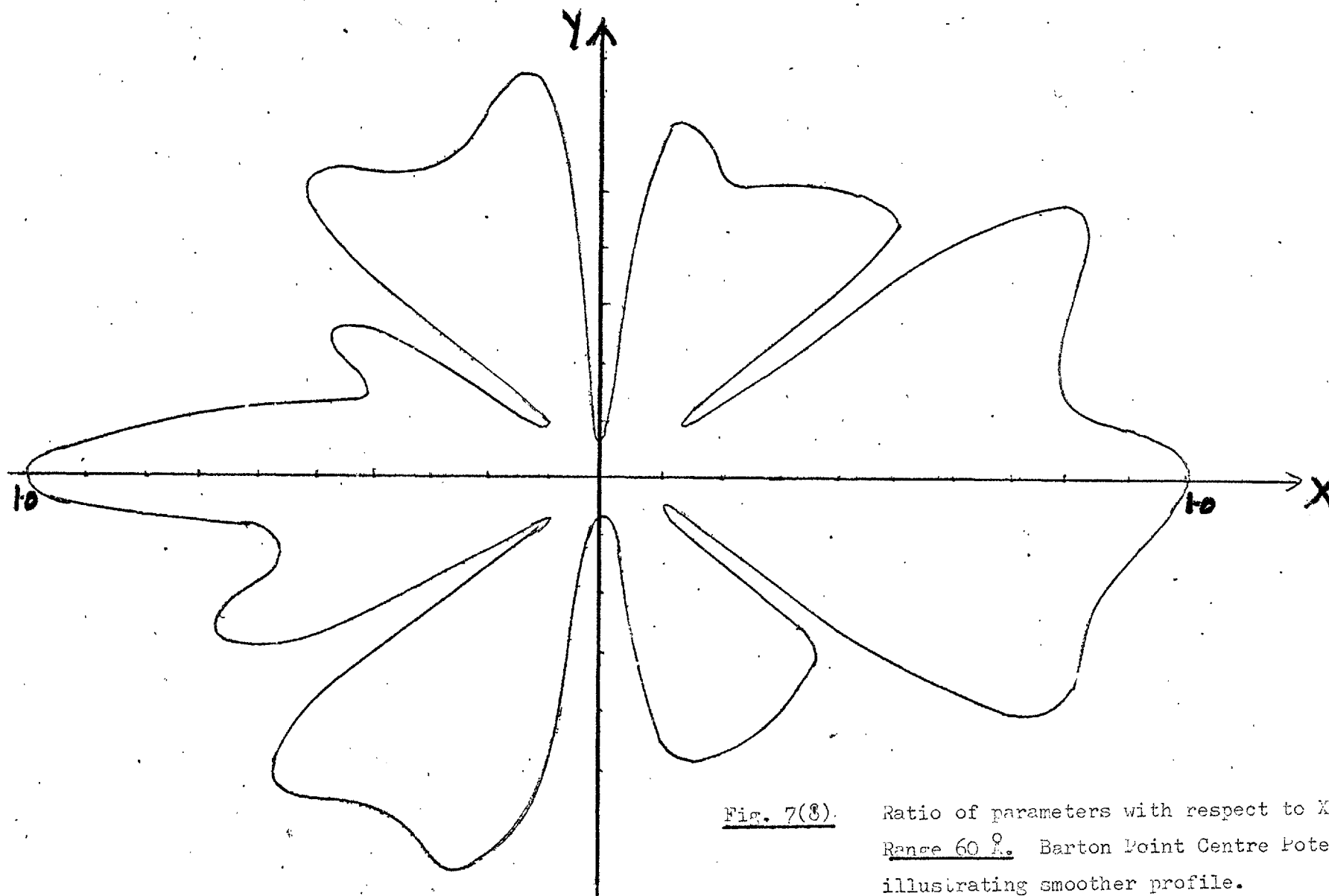
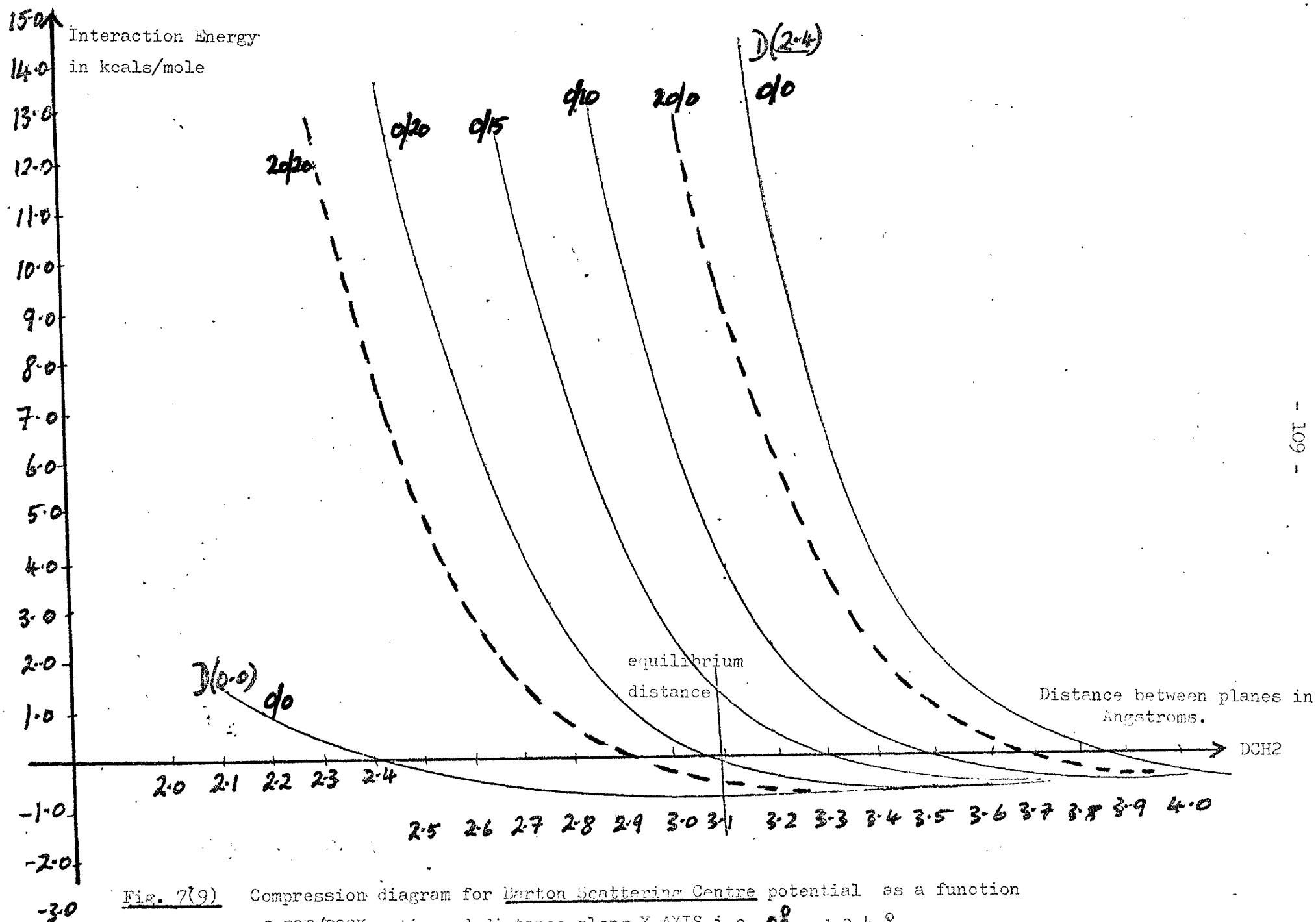


Fig. 7(8). Ratio of parameters with respect to X-AXIS.
Range 60 μ . Barton Point Centre Potential -
 illustrating smoother profile.



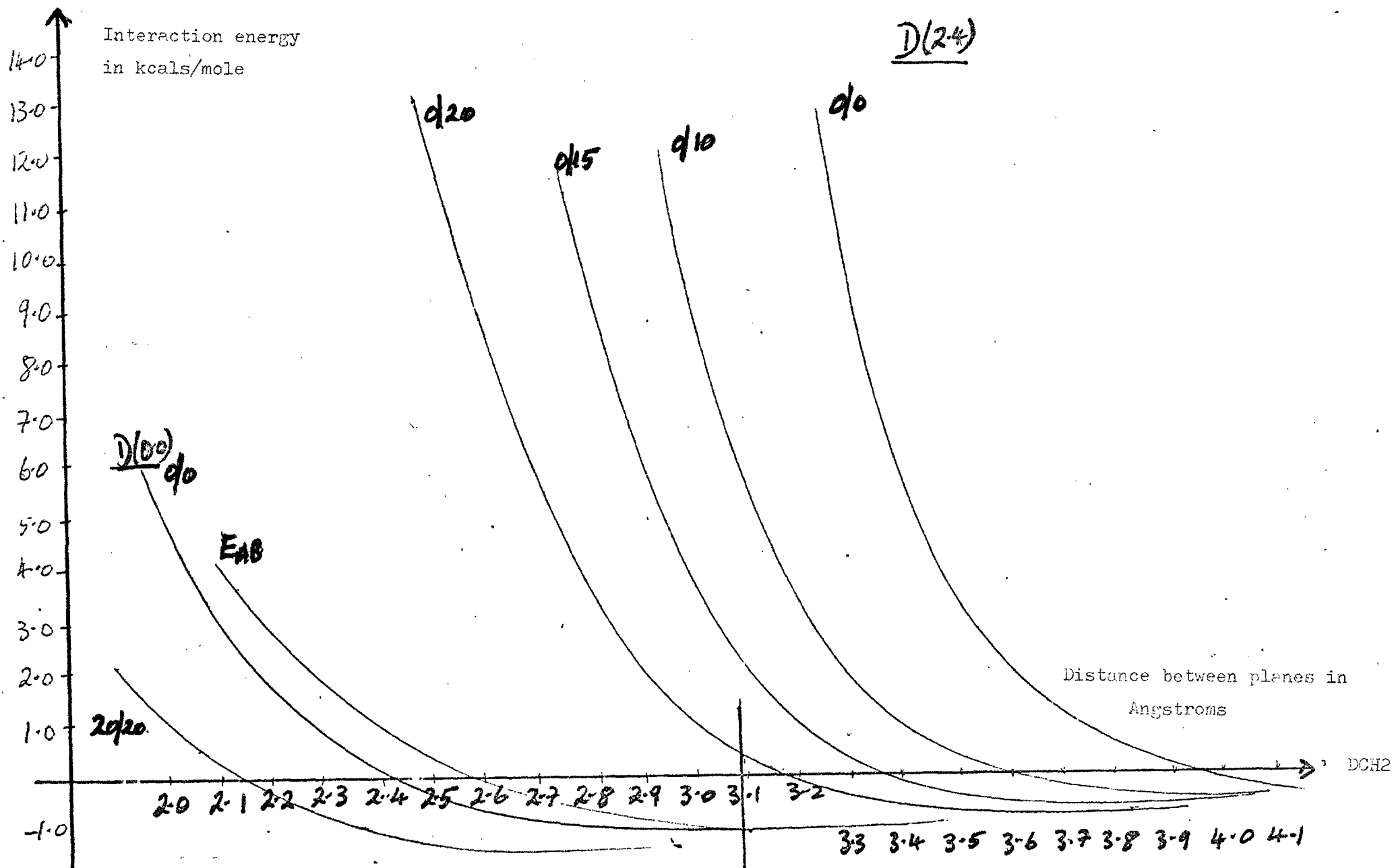


Fig. 7(10) Compression diagram of Slater Scattering Centre potential as a function of ROT/ROCK ratio and distance along X-AXIS i.e. OR and 2.4 Å

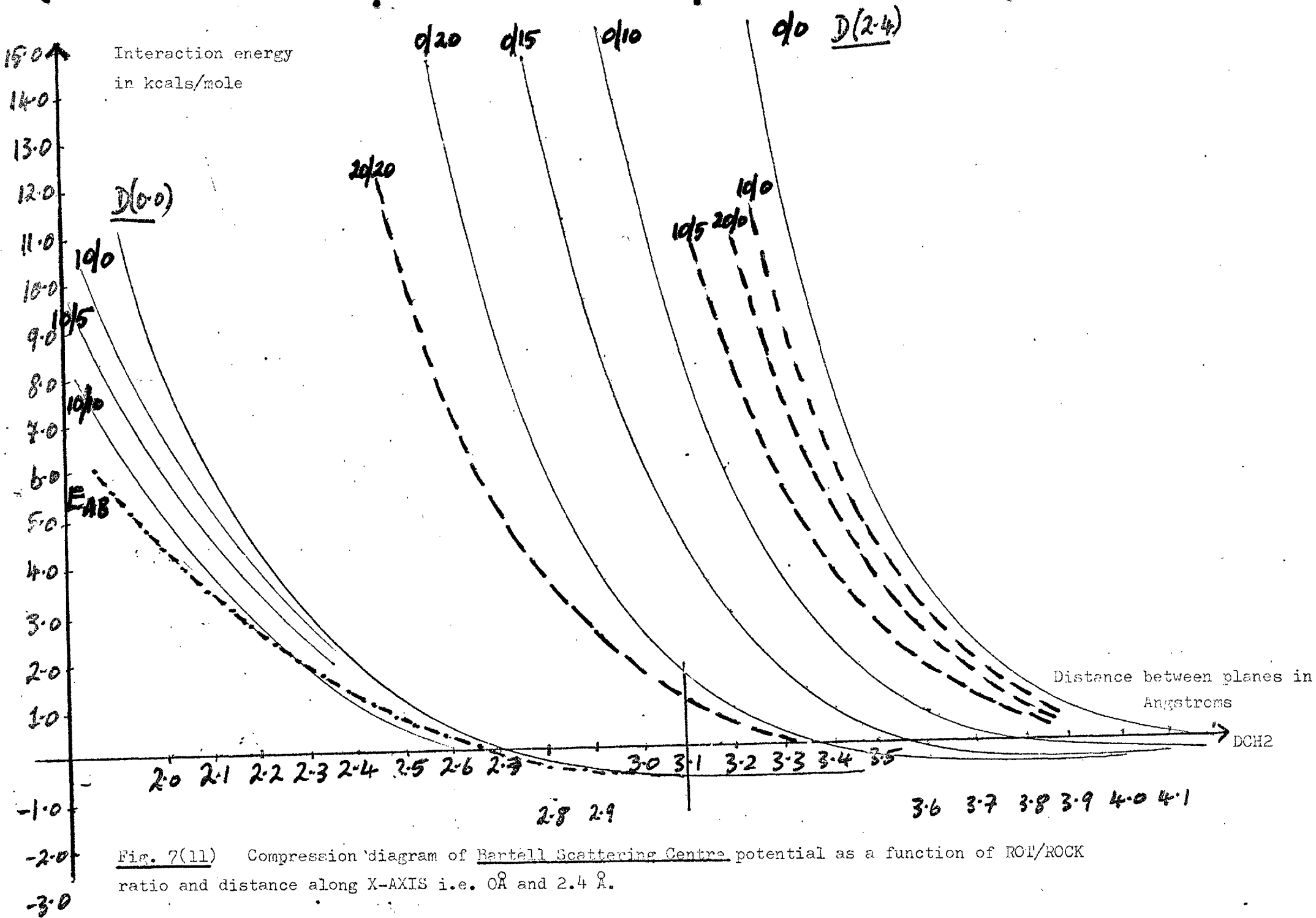


Fig. 7(11) Compression diagram of Bartell Scattering Centre potential as a function of $ROI/ROCK$ ratio and distance along X-AXIS i.e. $0\text{\AA}$ and $2.4\text{\AA}$.

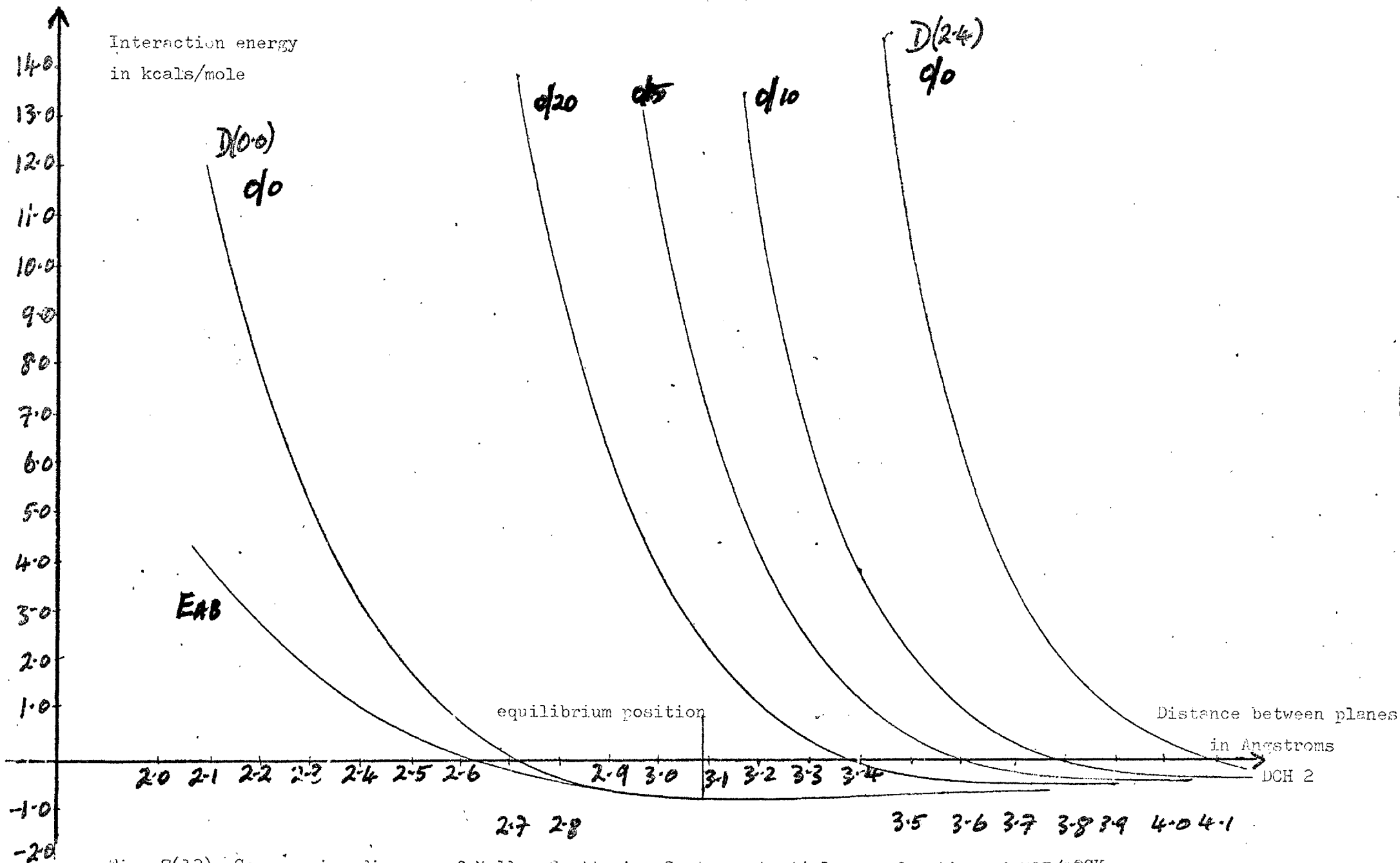


Fig. 7(12) Compression diagram of Muller Scattering Centre potential as a function of ROT/ROCK ratio and distance along X-AXIS. i.e. OR and 2.4 Å

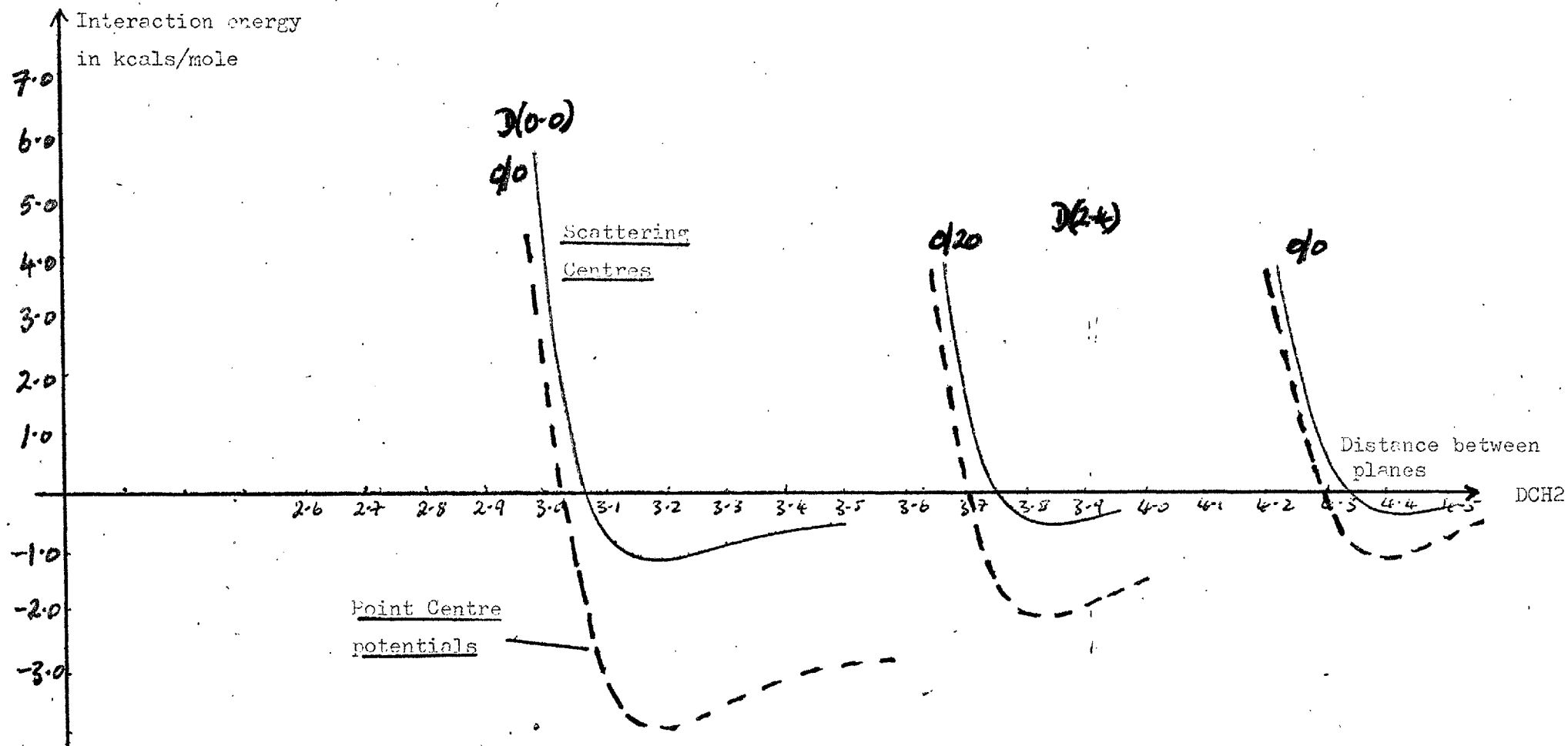


Fig. 7(13) Compression curve for fitted potential (monolayer - infinite layers) as function of ROT/ROCK ratio and distance along X-AXIS.

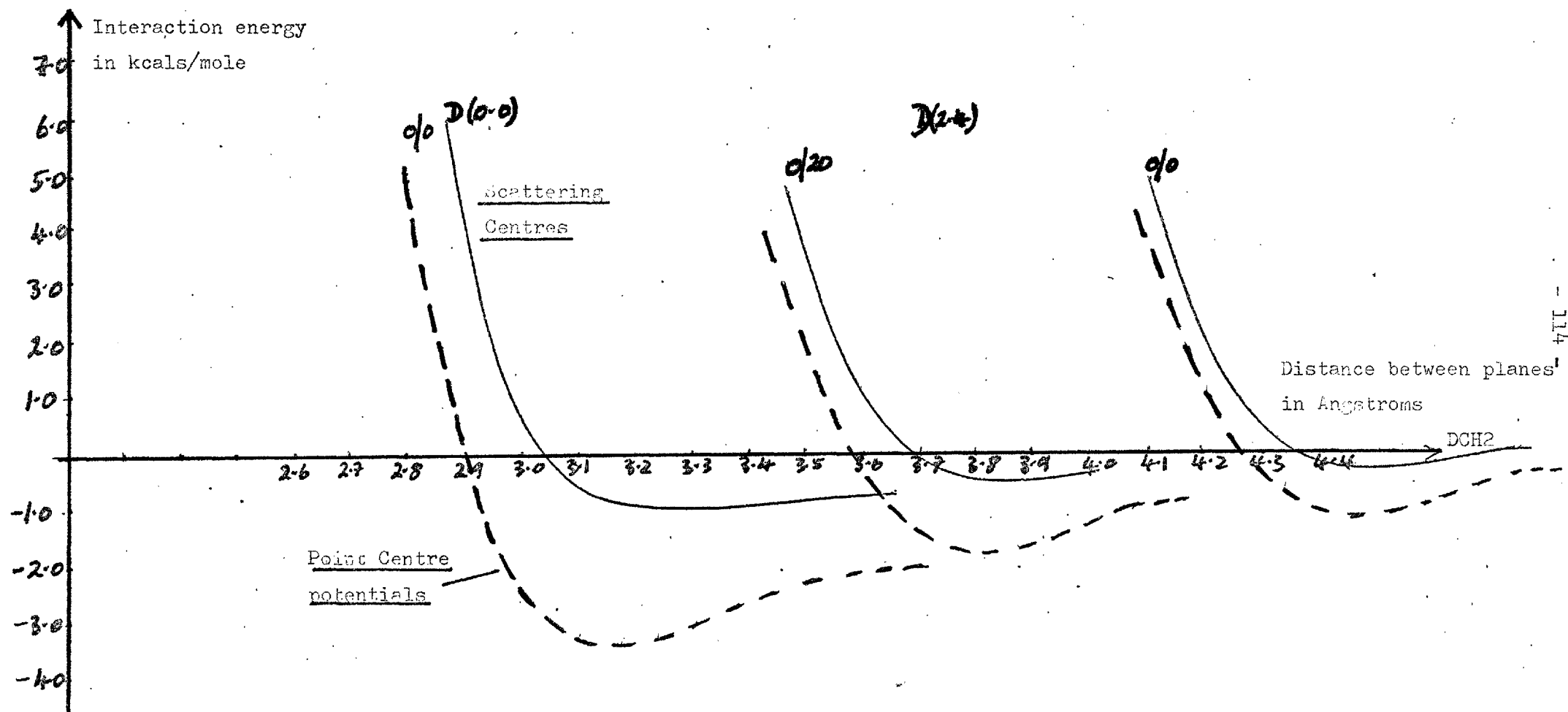
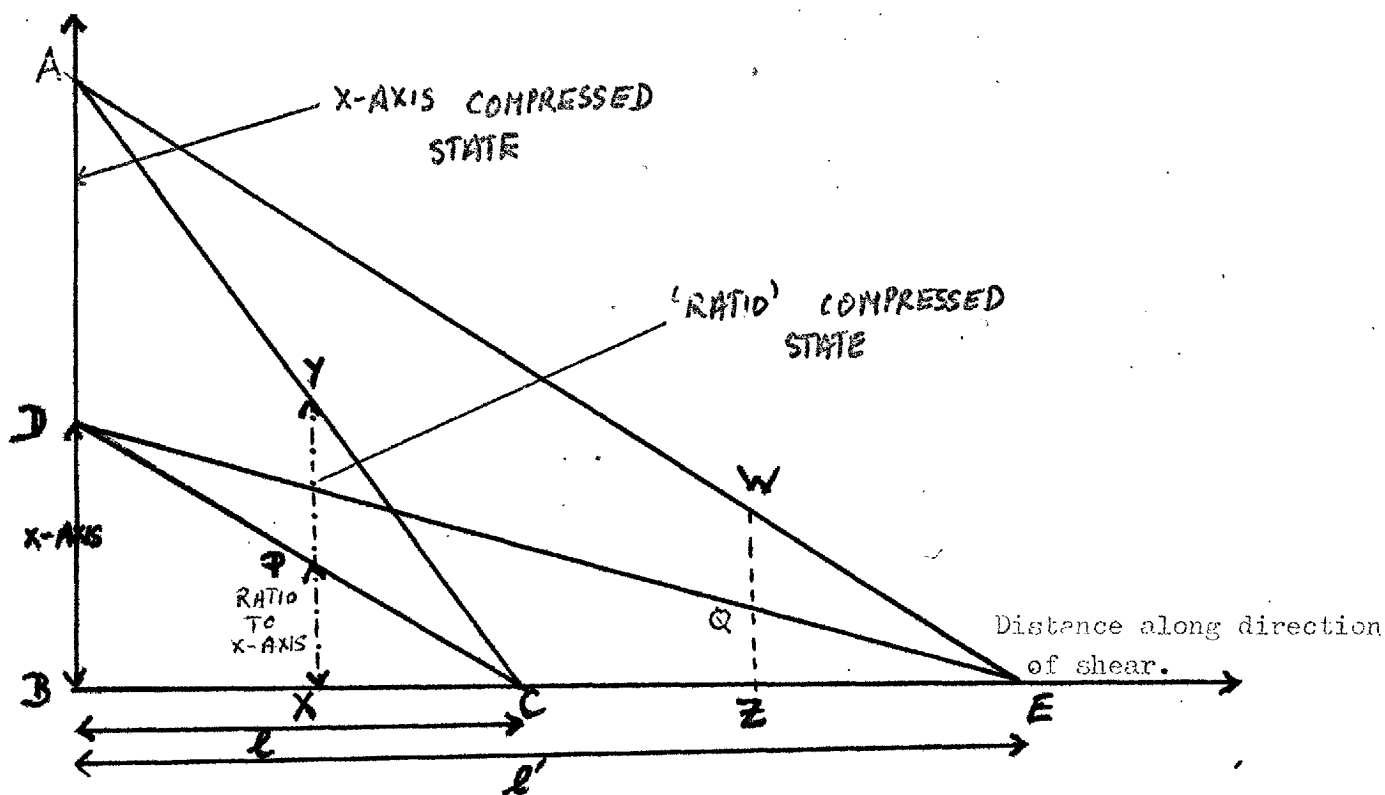


Fig. 7(14) Compression Curve of fitted potential (monolayer - finite layers) as a function of ROT/ROCK ratio and distance along X-AXIS.

Interaction Energy.



- (a) by similar triangles - DB: PX = AB : YX. Where DB represents X axis potential compared to ^{the} ratio to it; PX. AB represents either a new potential or a compressed state - and because the length l is taken to be the same, PX is increased to YX in the same ratio. The same is true if the force is calculated over the distance l' i.e. DB : QZ = AB : WZ.
- (b) Parameters from compression diagram.

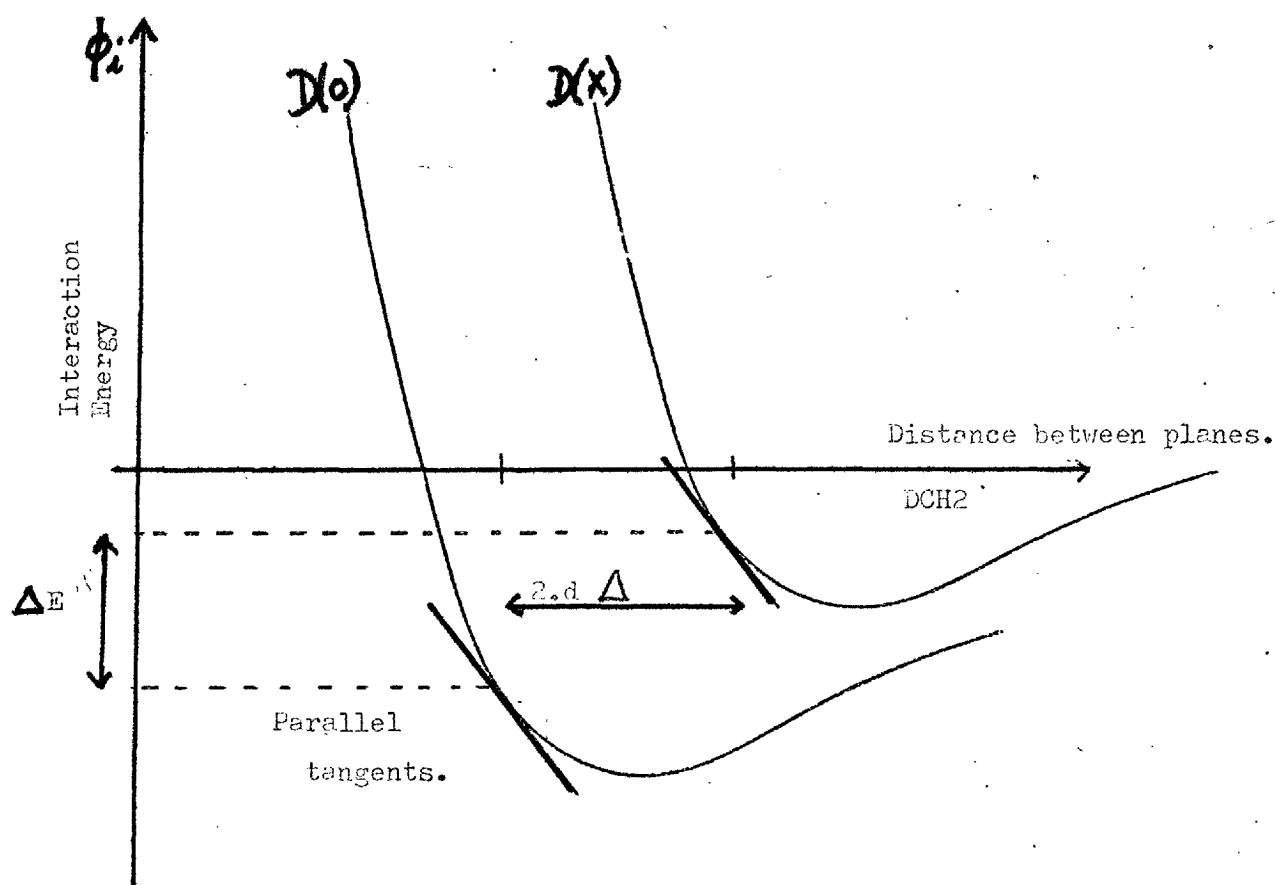


Fig. 7(15)

CHAPTER 8 - RESULTS

8.1 Results using Compressibility curves

By using figs 7(9-14) and equation (1), section 7.5, ΔE may be found for each potential as a function of load. The energy dissipated in kcal/mole/chain may be calculated by using the area of the chains, $20 \text{ \AA}^2$. Corresponding values of Δd in Angstroms can be read off the same diagrams. 'Static' and 'kinetic' friction forces value for the X-axis can be calculated by dividing ΔE by $1.4 \text{ \AA}$ and $7.46 \text{ \AA}$ respectively (the latter to find the energy dissipated/cm to enable the use of the averages over 360° , $7.46 \text{ \AA}$ is the length of the unit cell in the X-direction).

Using the tables presented in Chapter 6 relating compressive distributions, number of monolayers (N), potentials and pressure /0.1 Angstroms (P [0.1 $\text{\AA}$]), results were calculated as a function of

- a) Pressure
- b) Rotation (ROT/ROCK), Shift
- c) 'Static' and 'kinetic' friction
- d) X-AXIS value then averages.
- e) Finite and Infinite layers.

NB. (1) The energy associated with a Rotation of 20° is 0.5 kcal/mole or 0.38×10^{-13} ergs (4.3584×10^{-11} ergs = 627.23 kcal/mole). This can be expressed as $1.35 \times 10^3 \text{ kg/cm}^2$ and $0.25 \times 10^3 \text{ kg/cm}^2$ as the frictional force dissipated for 'static' and 'kinetic' in the X-direction.

(2) Errors

- (a) The main source of probable error is having to assume that all the energy is dissipated, hence the results express a maximum value.
- (b) An error of ± 0.025 kcal/mole when determining ΔE from graphs
- (c) $\pm 0.01 \text{ \AA}$ when determining Δd from graphs
- (d) The distribution associated with rotations - the above example assumes a sinusoidal one i.e. ROT (20) = 0.50 ± 0.15 kcal/mole
- (e) The compressive distributions - the results will express relative magnitudes.
- (f) The Area of the chain — $19.0 \pm 1.0 \text{ \AA}^2$

Example using polyfit Potential - 5M infinite - 1M finite layers

Using fig. 6(7) $p (0.1 \text{ \AA}) = 7.15 \times 10^4/\text{cm}^2$ for infinite layers.

Rotation ROT/ROCK = 0/20 on the X-AXIS.

Pressure	0	3.58	7.15	10.73	14.3
kcal/mole x 10 ⁴					
<u>AE</u>	0.325	0.30	0.30	0.30	0.30
kcal/mole	± 0.025	± 0.025	± 0.025	± 0.025	± 0.025
<u>AE</u>	11.0	10.4	10.4	10.4	10.4
ergs/cm ²	± 0.9	± 0.8	± 0.8	± 0.8	± 0.8
<u>F_E (STATIC)</u>	1.06	0.965	0.965	0.965	0.965
kg/cm ² x 10 ³	± 0.09	± 0.08	± 0.08	± 0.08	± 0.08
<u>F_E (KINETIC)</u>	0.20	0.18	0.18	0.18	0.18
kg/cm ² x 10 ³	± 0.02	± 0.02	± 0.02	± 0.02	± 0.02
<u>F_{LIFT} (ST)</u>	/	8.3	16.6	23.2	33.2
kg/cm ² x 10 ³	/	± 0.8	± 1.6	± 2.3	± 3.3
<u>F_L (K)</u>	/	1.56	3.12	4.35	6.24
kg/cm ² x 10 ³	/	± 0.15	± 0.3	± 0.44	± 0.62
<u>ROCK (20) ST</u>	1.35				
kg/cm ² x 10 ³	± 0.45				
<u>ROCK (20) K</u>	0.25				
kg/cm ² x 10 ³	± 0.08				
<u>F_{ST}</u>	2.41	10.615	18.915	25.515	35.515
kg/cm ² x 10 ³	± 0.45	± 0.8	± 1.7	± 2.5	± 3.5
<u>F_K</u>	0.45	1.995	3.56	4.8	6.65
kg/cm ² x 10 ³	± 0.08	± 0.16	± 0.33	± 0.46	± 0.65

Fig 8(1) was drawn and $\mu_{ST} = 0.23 \pm 0.07$ and $\mu_K = 0.044 \pm 0.012$
N.B. The finite monolayer will have the same parameter μ - but a differing load system as p(0.1 Å) is different.

The results obtained can be summarised in the following tables.

Table (1)

Rotation 0/0 - Static - X-AXIS

M = no of layers

Fo = intercept of FN curves in kg/cm² x 10³

Potential	Infinite layers	Fo	μ	Finite layers
Barton	50 - 100 ^M	2.083 ± 0.09	0.50 ± 0.05	5 ^M
Hendrickson	50 - 100 ^M	1.596 ± 0.09	0.50 ± 0.05	5 ^M
Slater	11 ^M	0.965	0.49	3 - 5 ^M

Table (1) Continued

Potential	Infinite layers	Fo	μ	Finite layers
		± 0.09	± 0.05	
Bartell	11 ^M	1.74	0.40	3 ^M
		± 0.09	± 0.04	
Muller	9 ^M	1.74	0.470	3 ^M
		± 0.09	± 0.045	
Len-Jones	7 - 9 ^M	0.675	0.480	3 ^M
		± 0.09	± 0.045	

Table (2)

Rotation 0/0 - Kinetic - X-AXIS

Potential	Infinite layers	Fo	μ	Finite layers
Barton	50 - 100 ^M	0.393	0.094	5 ^M
		± 0.02	± 0.01	
Hendrickson	50 - 100 ^M	0.393	0.094	5 ^M
		± 0.02	± 0.01	
Slater	11 ^M	0.180	0.10	3 - 5 ^M
		± 0.02	± 0.01	
Bartell	11 ^M	0.326	0.08	3 ^M
		± 0.02	± 0.01	
Muller	9 ^M	0.328	0.085	3 ^M
		± 0.02	± 0.01	
Len-Jones	7 - 9 ^M	0.128	0.09	3 ^M
		± 0.02	± 0.01	

Table (3)

0/20 STATIC X-AXIS

Potential	Infinite layers	Fo		Finite layers
Barton	50 - 100 ^M	2.22	0.25	5 ^M
Hendrickson	50 - 100 ^M	2.22	0.25	5 ^M
Slater	11 ^M	2.22	0.3	3 - 5 ^M
Bartell	11 ^M	2.02	0.15	3 ^M
Muller	9 ^M	2.7	0.325	3 ^M
Len-Jones	7 - 9 ^M	2.02	0.215	3 ^M
Polyfit	5 ^M	2.41	0.23	1 ^M
Polyfit	3 ^M	2.71	0.23	1 ^M

Errors ± 0.45 for Fo and ± 0.07 for μ

Table (4)

0/20 KINETIC - X-AXIS

<u>Potential</u>	<u>Infinite layers</u>	<u>Fo</u>	<u>μ</u>	<u>Finite layers</u>
Barton	50 - 100 ^M	0.43	0.047	5 ^M
Hendrickson	50 - 100 ^M	0.43	0.047	5 ^M
Slater	11 ^M	0.43	0.055	3 - 5 ^M
Bartell	11 ^M	0.394	0.03	3 ^M
Muller	9 ^M	0.55	0.04	3 ^M
Len-Jones	7 - 9 ^M	0.394	0.04	3 ^M
Polyfit	5 ^M	0.45	0.044	1 ^M
Polyfit	3 ^M	0.50	0.039	1 ^M

Errors - ± 0.08 for Fo and ± 0.012 for

The last table can be summarised as follows - by taking the averages of the layer number and using the average (70%) of the Fo value calculated in the previous chapter. The average of exponential polyfit potentials are used.

Table (5)

<u>Infinite layers</u>	<u>Fo</u>	<u>70% Fo</u>	<u>Finite layers</u>
50 - 100 ^M	0.43	0.305	5 ^M
(11 - 0) ^M	0.442	0.309	
5 ^M	0.45	0.315	3 ^M
3 ^M	0.50	0.350	1 ^M

Table (5) is reproduced in figs 8(2). An inverse compressive function ($f [1/d]$) has been used - the graphs have been extrapolated to enable the relationship between parameters to be seen more clearly.

Programs were also run to obtain compressive data on the X-AXIS utilizing SHIFT (20). Results are summarised in Table (6). See fig. 8(3)

Table (6)

0/0 - Shift (20) - X-AXIS

<u>Infinite layer</u>	<u>DE kcal/mole</u>	<u>Δd</u>	<u>Fo kg/cm² x 10³</u>	<u>Finite layers</u>
100 ^M	0.15	0.428	0.079	5 ^M
11 ^M	0.11	0.43	0.058	5 ^M
11 ^M	0.125	0.42	0.067	3 - 5 ^M
9 ^M	0.15	0.40	0.079	3 ^M
5 - 3 ^M	0.175	0.35	0.093	1 ^M

The Coefficients of Friction are all in the range 0.03 - 0.05

8.2 Effect of other compressive distributions

All the information in Tables (1) - (6) represent an inverse compression distribution. As the coefficient of friction and F_o are shared by infinite and finite layers, and μ depends on (ad/X) to a first order approximation, an inverse square distribution, compressive distribution, can be attributed to each potential combination. This implies that the parameters F_o and μ will be the same but the number of layers represented by a given combination will differ. Fig. 8(4) shows some Force-Load systems referred to in the tables.

Programs were also run using Cameron's isotropic compressive case of 40, 80 and 120 ton/sq" using the elastic constant E_{AB} (i.e. (1) the a and b directions of the unit cell (2) DCH2 values of 2.85 Å, 2.65 and 2.45 Å). All these programs yielded straight line graphs, figs. 8(5), as a function of rotation.

8.3 Results using Shear, Rotations and Shift

In section 7.2 the programs run were described and the results and graphs obtained are given below.

① Using an anisotropic compression function ($f [1/d]$), infinite layers, rotation 0/20, for the X-AXIS then using the Root Mean Square value of 0.63 to find the average over 360° and approximately 0.1 to find a minimum value along a diagonal of the unit cell.

Layers	$F_o (X) \times 10^3$	$F_o (AV) \times 10^3$	$F_o (MIN) \times 10^3$	$\mu (MIN)$
(100 - 50)M	0.827	0.525	0.245	≈ 6
9 - 11 M	1.10	0.690	0.375	≈ 0.42
7 - 5 M	3.9	2.4	1.26	≈ 1.1

It can be seen that F_o follows the trend of fig. 8(2) and 8(3). Values of μ MIN are unreliable and the general shape of the Force-Load curve is asymptotic at large loads. The case of infinite layers at light loads being the only case where the gradients are approximately straight. See fig. 8(6).

For example the energy barrier for a Barton-Scattering centre potential, rotation 0/0 (rigid), and zero pressure is 20.49 - using 0.1X along the diagonals - which approximately gives a value of 3.0×10^3 kg/cm² for F_o .

② Isotropic Compression

Programs were run using pressures of 0, 40, 80, 120 ton/sq" with scattering centre potentials. By using the relationship $-\Delta\lambda = (p/E_c)$, where $\Delta\lambda$ is the compressive strain, p is the pressure

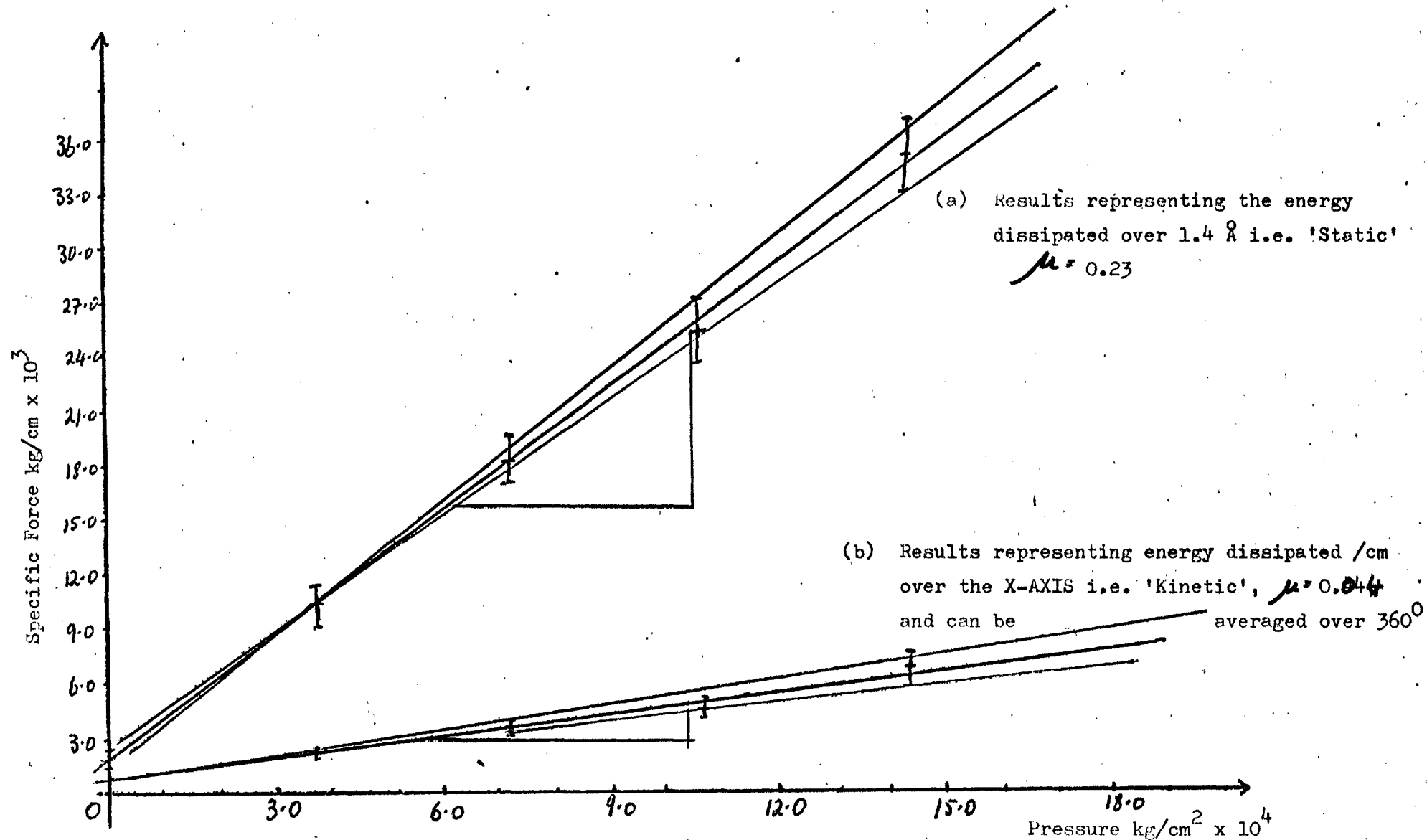


Fig. 8(1) - Specific Force against pressure for a Polyfit fitted potential representing a monolayer (finite layers) for a rotation of 20° on the X-AXIS of the unit cell.

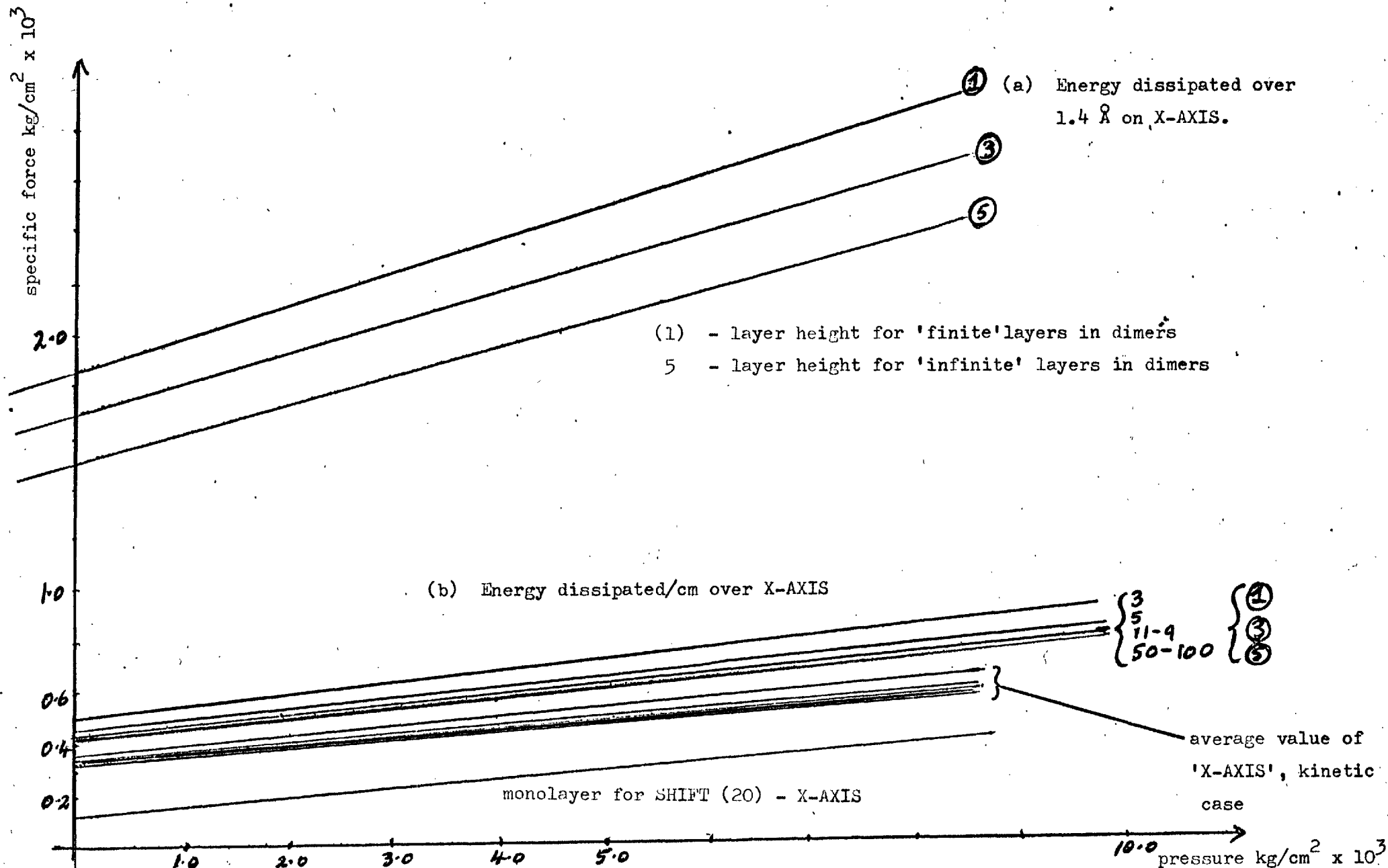


Fig 8(2) - Graph of specific force against pressure as a function of layer height, rotation, X-AXIS and average value.

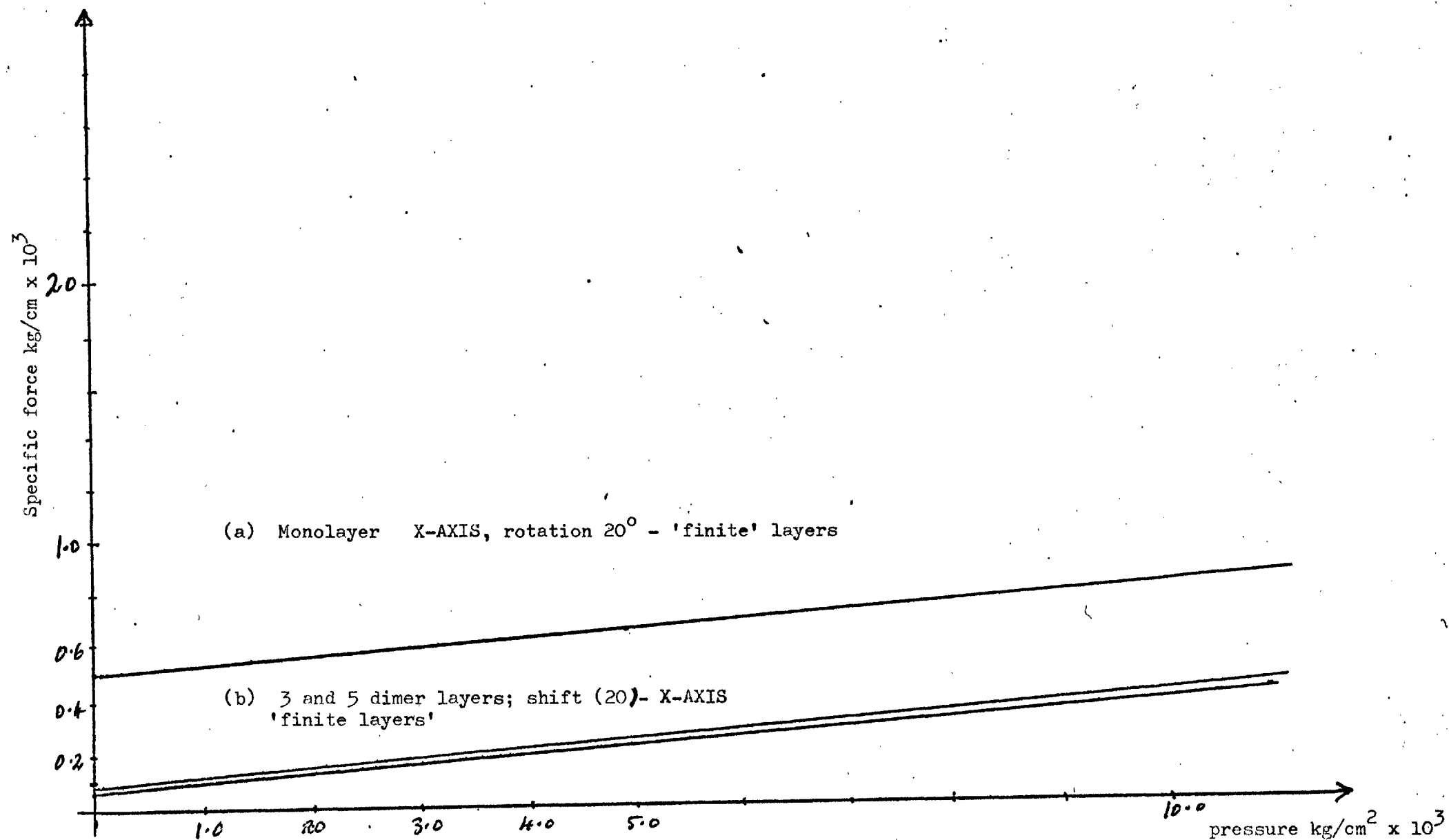


Fig. 8(3) - Graph of specific force against pressure as a function of layer height, rotation and shift of chain to vertical.

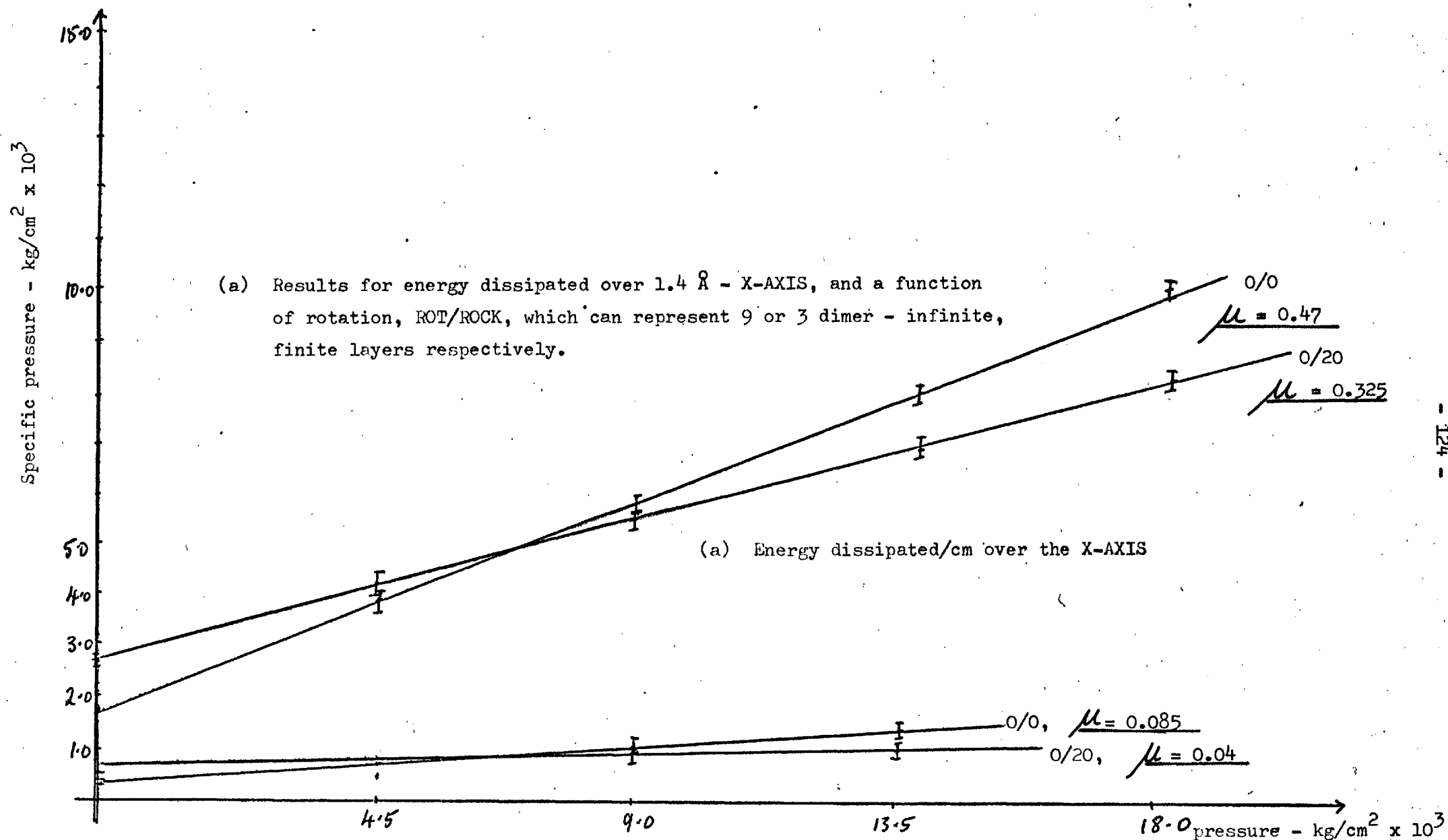


Fig. 8(4) - Graph of specific force against pressure for a Muller - Scattering Centre potential as a function of rotation and energy dissipation.

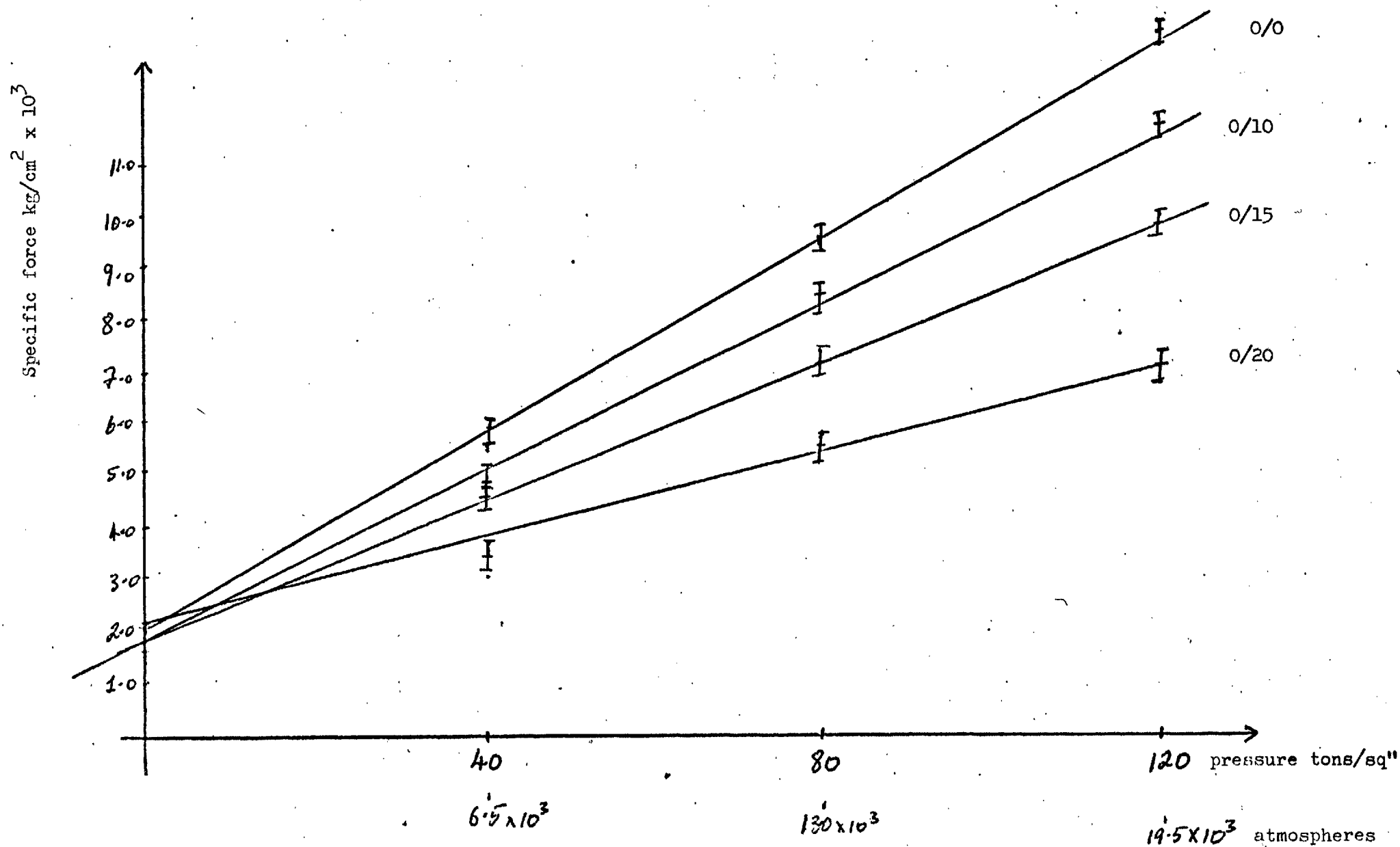


Fig. 8(5) - Specific force against pressure for a Slater Scattering Potential as a function of rotation.

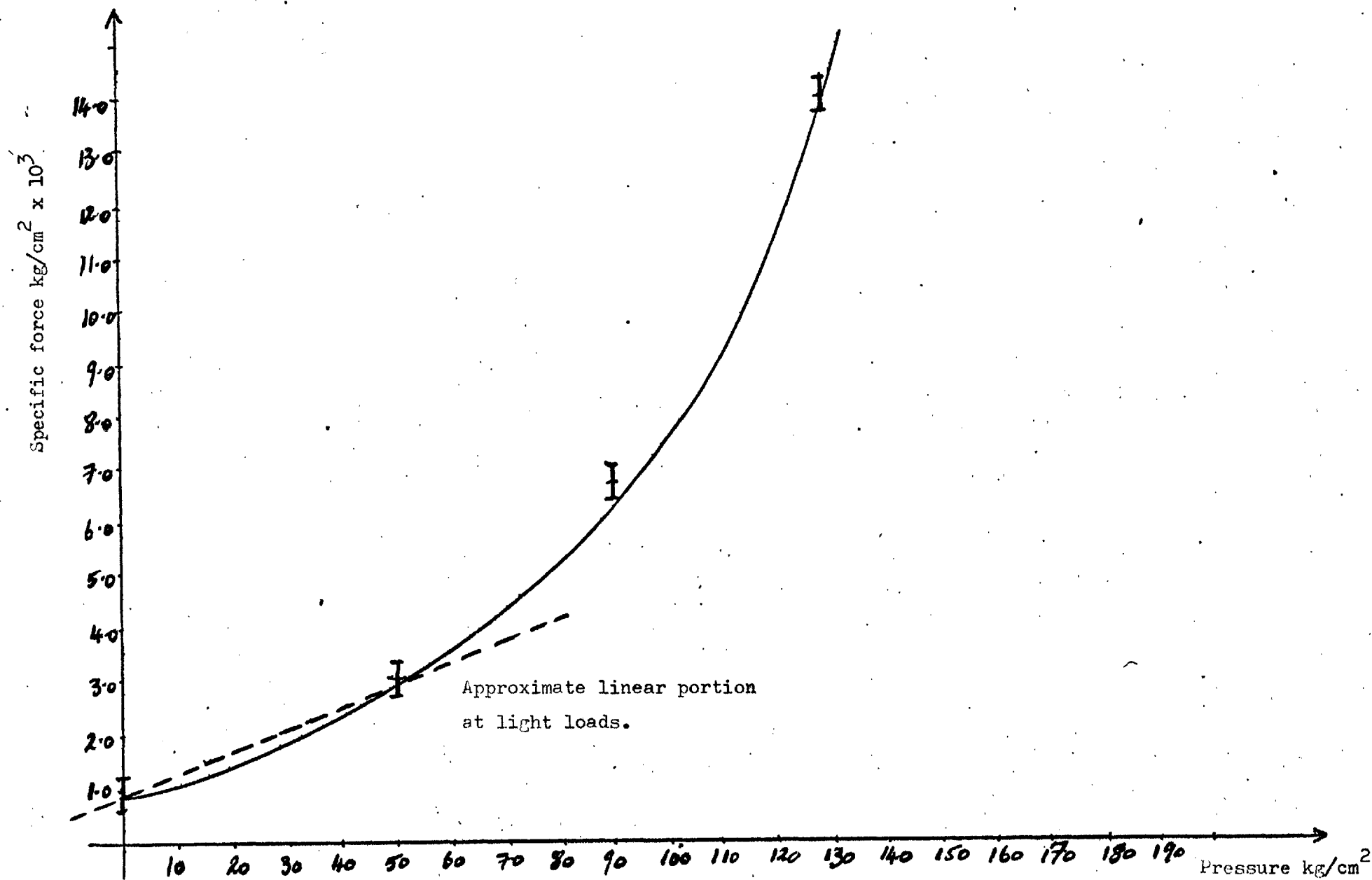


Fig. 8(6) - Force-Load diagram for a Barton-Scattering centre potential; rotation of 20° ; anisotropic compression, $f(1/d)$ - infinite layers.

and E_c is the modulus of compression in the Z direction of a monolayer - $(3.33 \times 10^{10} \text{ dynes/cm}^2)$, the decrease in gap distance from $3.09 \text{ \AA}$ for a load of 40 tons/sq" is $0.00618 \text{ \AA}$. (i.e. $DCH2 = 3.8382 \text{ \AA}$). All the potentials were subjected to this method and for a rotation of $0/20$ over the X-AXIS typical results were as follows. (ΔE is the potential profile to be overcome in kcal/mole).

Potential	ΔE as a function of load (kcal/mole)			
Barton	0.946,	0.970,	0.998,	1.028
Slater	1.376,	1.412,	1.452,	1.492
Bartell	2.158,	2.232,	2.296,	2.370
Muller	3.776,	3.902,	3.996,	4.122
Len-Jones	4.736,	4.890,	5.108,	5.274

The results can be summarised in the following table - $F_o(X)$ is the intercept in $\text{kg/cm}^2 \times 10^3$ of the Force-Load Graphs (straight lines could be drawn through the points for rotations of $0/0$ (rigid), $0/10$ and $0/20$) - figs. 8(7), 8(8) and 8(9). The minimum value is approximately 30% of the X-AXIS kinetic values along the diagonals of the cell - the potentials are scattering centre approximations and μ_{ST} is the coefficient of 'static friction' on the X-AXIS

Potential	$F_o(X)$	$F_o(MIN)$	μ_{ST}
Barton	1.07	0.32	0.023
Slater	1.42	0.42	0.030
Bartell	2.08	0.62	0.055
Muller	3.51	1.05	0.088
Len-Jones	4.20	1.25	0.130

If an average of the exponential potentials is taken; $F_o(MIN) = 0.64 \times 10^3 \text{ kg/cm}^2$. For 'Static' conditions over the X-AXIS the average coefficient of friction is 0.065 and for 'kinetic' conditions $\mu = 0.02$. There is an error of ± 0.002 in ΔE when reading from the computer print outs and $\pm 0.05 \text{ \AA}$ in 'X' for 'static' cases i.e. $1.4 \pm 0.05 \text{ \AA}$.

③ Shift (20°) ; Rotation $0/0$ and $0/5$

Results were obtained for shift (20) and a slight rotation of the molecules. Only F_o values are compared - for the general shape of the Force-Load curve is similar to fig. 8(6). Averages were taken using the tables in section 7.4

i.e. Potential (S.C.)	0/0 F ₀		0/5 F ₀	
	X AXIS	MIN (DIAG)	X AXIS	MIN (DIAG)
Barton	1.3	0.78	0.8	0.75
Bartell	2.6	1.46	1.3	1.25
Slater	1.9	1.0	0.95	0.9
Muller	5.0	3.0	2.5	2.4

It can be seen that the minimum values are approximately equal in both cases - but the magnitudes are far larger than the results in Table (6) and μ is unreliable.

All the results are discussed in terms of present theories in the next Chapter.

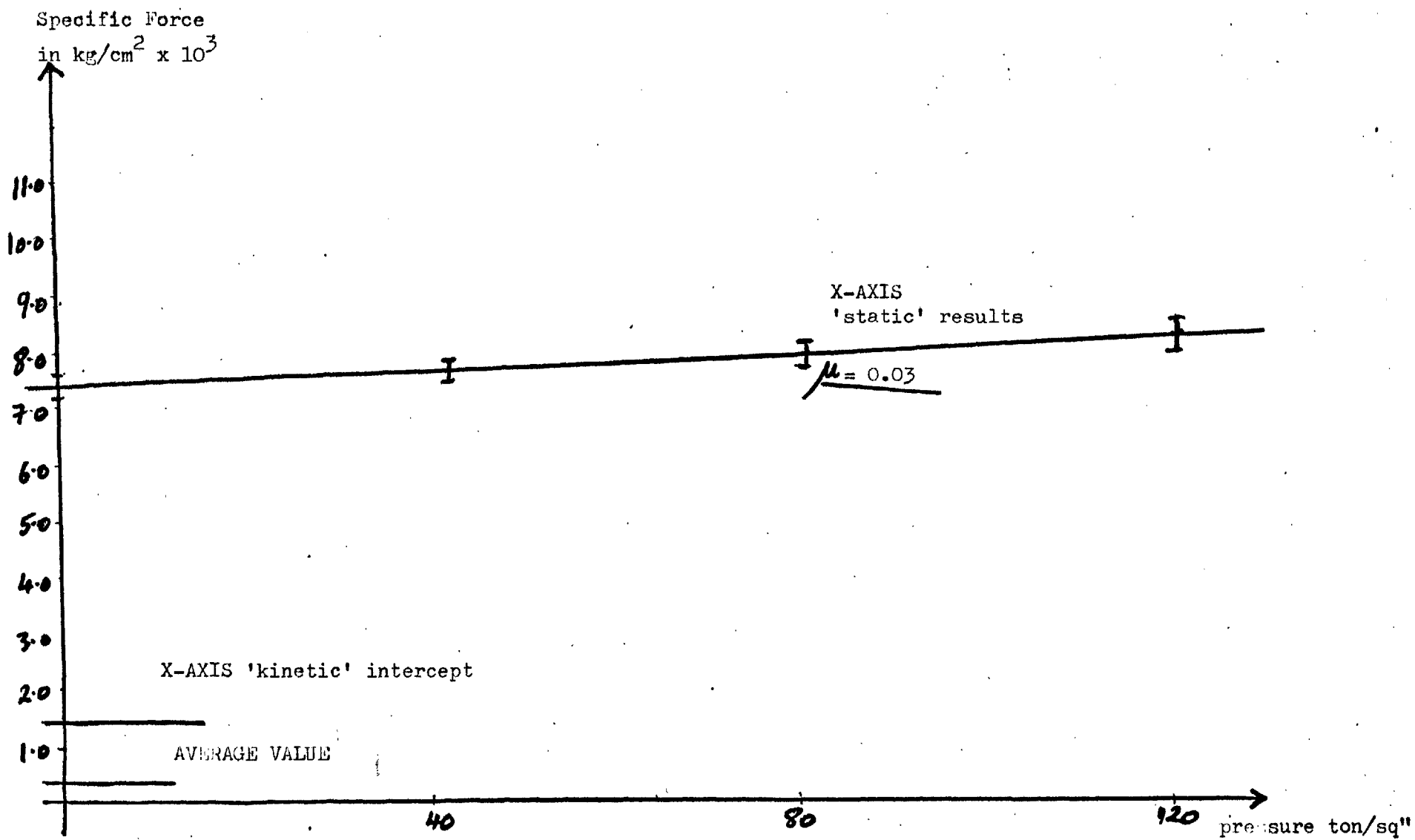


Fig 8(7) - Slater Scattering Potential results for a rotation of 0/20 using $E_c = 3.33 \times 10^{10}$ dynes/cm²

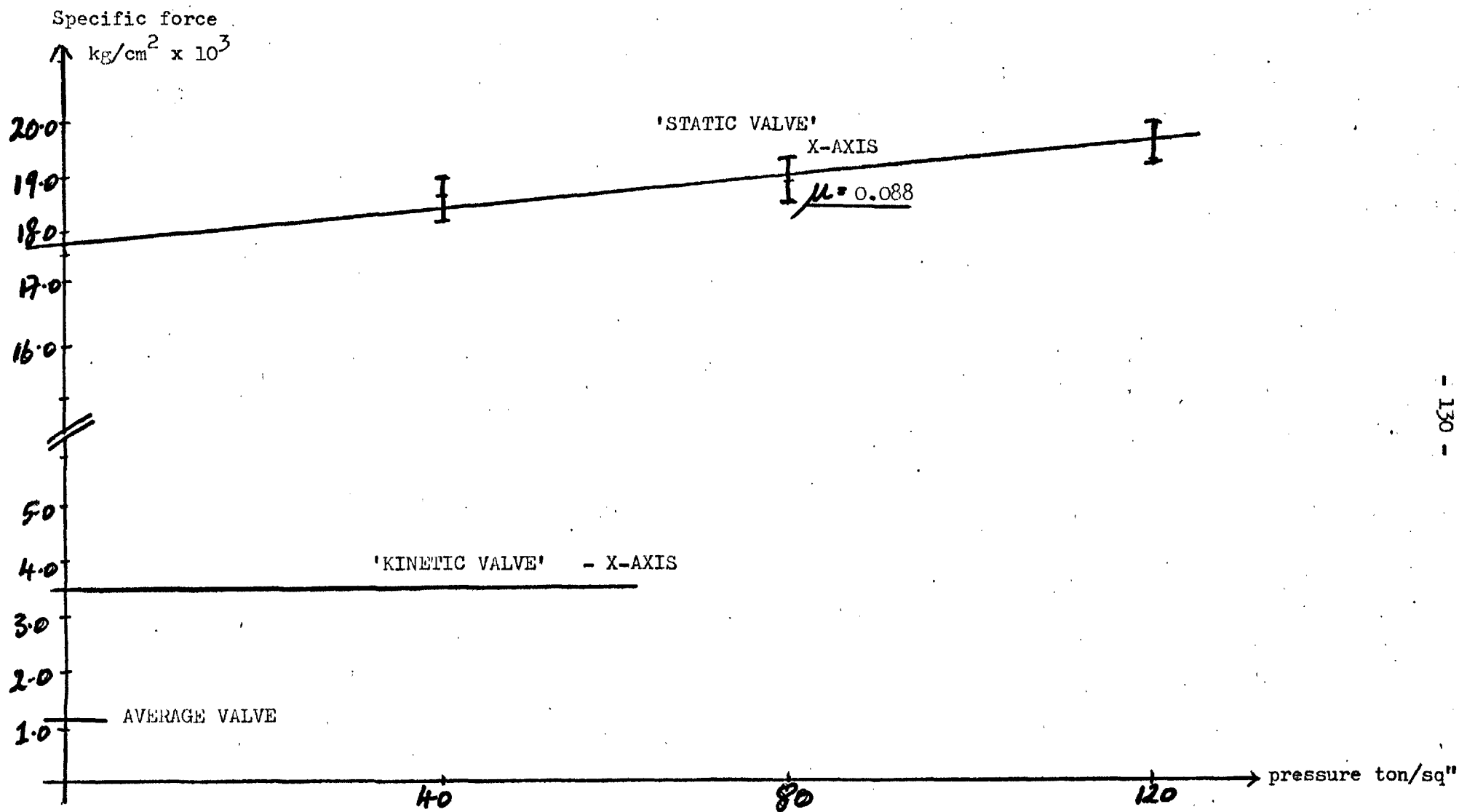


Fig. 8(8) - Muller Scattering Potential result for a rotation of 0/20 using $E_c = 3.33 \times 10^{11}$ dynes/cm²

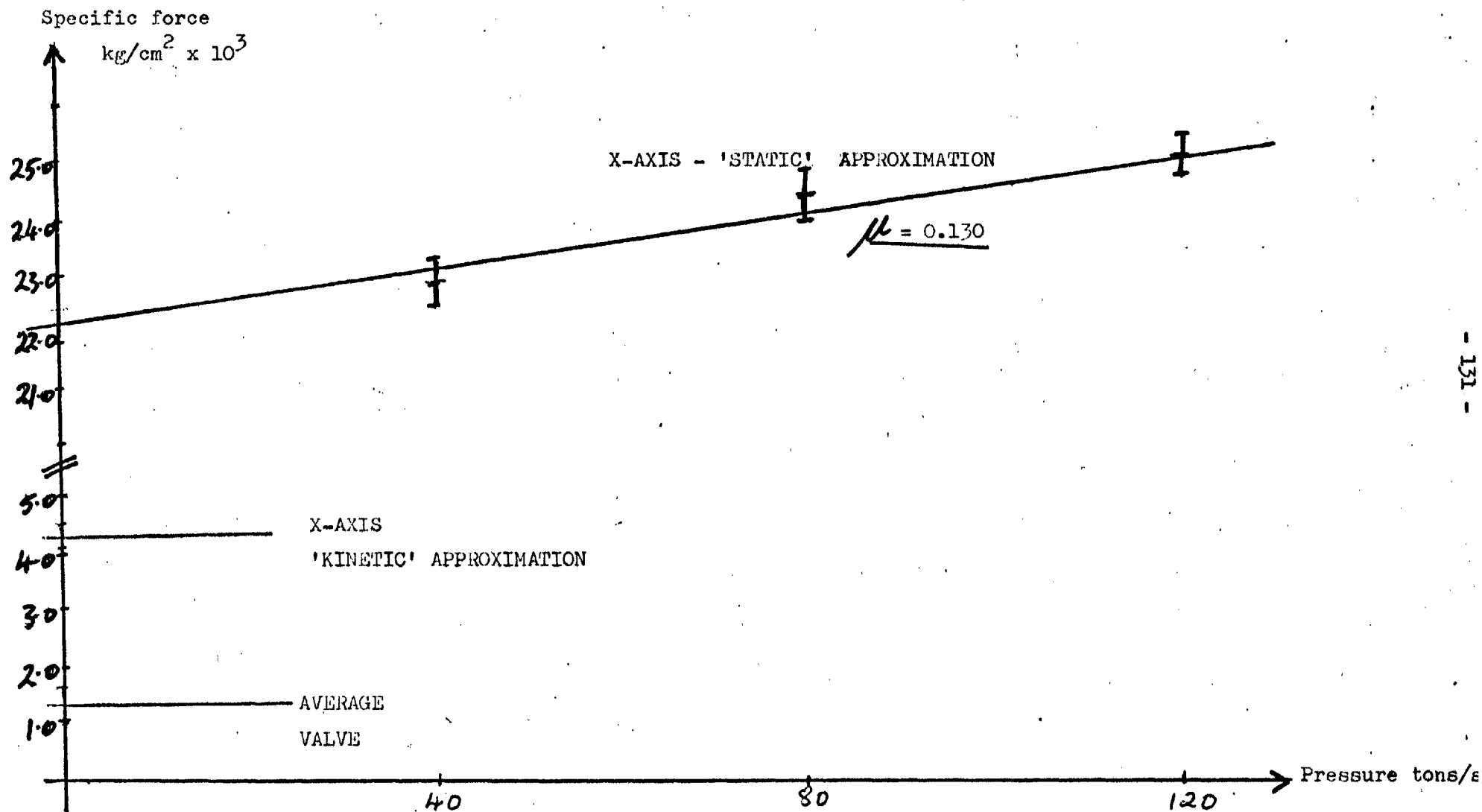


Fig. 8(9) - Len-Jones Scattering Potential results for a rotation of 0/20. - $E_c = 3.33 \times 10^{11}$ dynes/cm²

CHAPTER 9 - DISCUSSION

9.1 Shear as a function of Rotations and Inclination

Bowden and Tabor (1) quote Bridgman's work on the effect of pressure on organic materials i.e. the specific shear strength increases almost linearly with the pressure. Akhmatov (2) quotes the work of Boyd and Robertson with regard to the shearing properties of stearic acid i.e. the coefficient of friction changes from 0.01 to 0.05 as a function of pressure - and the lowest average is 0.022.

In the previous chapter three types of results were considered -

- (a) Using an anisotropic compression function, variable coefficients were obtained - see fig. 8(6) - but these were unreliable and in magnitude far too high. The shape of the curve appears to be asymptotic at high pressures - ref (2)
- (b) By considering all the potential systems with isotropic compressions using Young's Modulus equals 3.33×10^{11} dynes/cm² - fig. 8(7).

Using an average of exponential functions a value of approximately 0.02 for μ was calculated for the X-AXIS.

- (c) When inclining the chains to the vertical results similar to (a) were obtained and values of F_0 were approximately equal as a function of rotation and diagonal of the unit cell. Godfrey (3) gives several values for the shear stress of stearic acid as a function of pressure ranging from 25 kg/cm² at 250 kg/cm² of pressure to 140 kg/cm² at pressures of 1000 kg/cm² and 440 kg/cm². It can be seen that values of F_0 are generally too high assuming all the energy is dissipated.

Fig 9(1) shows the effect of rotation across the X-AXIS for SET (44) - when the energy of rotation is considered, the minimum energy dissipation is ⁱⁿthe range 10° - 25°.

9.2 Compressibilities and Shear

The results and method of calculation using the compressability diagrams - figs. 7(9 - 14) were described in Section 8.1 Figs 8(2) and 8(3) show the same trend as fig. 1(1) with respect to the layer height when considering the anisotropic compression functions; $f(1/d)$ and $f(1/d^2)$. The Coefficients of Friction are of the right order (0.08 - 0.03) but again F_0 is too high. No matter what compressive distribution is used the coefficient of friction was a constant value as a function of pressure.

These two sections have shown that by using different distributions different traits of fatty acids films are shown, which are all claimed in the literature. All these processes can probably occur depending on external conditions which will cause certain situations to predominate i.e. structural differences in the crystal planes.

9.3 Applicability of Potentials

As demonstrated in earlier chapters the Scattering centres approximation for attractive potentials gives a more complete picture than the point centre potentials. Each potential can be used to describe a particular layer height - although the softest potential, Barton, only approximated to 100 - 50 monolayers. The very nature of shear and hence boundary friction has been shown to be governed by the repulsive contributions and adhesion by the attractive forces.

9.4 Results as a function of layer height

The similarity of the results to fig. 1(1) has been shown. The force of friction is sensitive to the type of distribution used - this implies extreme sensitivity to repulsive potentials. Any dislocations in the system will affect the results from the maximum values obtained. Wert and Thomson (4) state that pure crystals with only a few dislocations deform plastically at an order of four or five magnitudes less than their shear moduli. This, together with any change of the maximum nature of energy dissipation would alter the magnitude of F_0 .

Sometimes a 'pack of cards' model is used to explain shear in boundary layers. This assumes that all the methyl planes slip over each other at the same rate, as a function of layer height. This means that for an isotropic compressive case the methyl distances all decrease an equal amount, so when different layer heights are sheared the least resistance will be displayed by a monolayer, at a certain pressure. This is contrary to figs. 1(1), 8(2) and 8(3). If an anisotropic function is used, shear implies relative motion of the dimer planes i.e. viscosity effects.

9.5 Surface Roughness

Kragelskii (5) quotes results as a function of surface roughness, load, thickness and coefficient of friction - fig. 9(2). This can be explained as follows -

- (a) Portion AB - roughness can be represented by fig. 9(3) - more specifically by the ratio (τ / R_{MAX}) . Thus when the Roughness increases this ratio decreases. It also appears in expressions for surface area calculations (5) and is thus proportional to the force of friction (equation (5) - Chapter 1). So when the roughness increases μ will decrease.
- (b) Portion BC - For a particular layer height as the surfaces get rougher, thinner layers will be involved in any friction process. From figs. 8(2) and 8(3) there is larger friction force associated with thinner layers - thus μ increases.

9.6 Theories of Boundary Friction

Two main points arise from all the specific force - pressure diagrams,

- (a) Coefficients of friction of fatty acids sliding on itself are of the right order 0.1-0.02
- (b) In all cases for zero load there was an intercept on the Force ordinate.

These are discussed in relation to theories, light loads and adhesion in the next two sections.

9.7 Adhesion

Adhesion of molecular layers can be regarded by two arguments.

- (a) Adhesion can be thought of as arising from the reverse of compression i.e. ~~tension~~ - fig. 9(4). The position of the ultimate breakdown point is not known, but along the slip plane seems reasonable. For all the potentials ϕ_0 is approximately the same i.e. as a function of layer height, and the adhesion force is proportional to (ϕ/D) . The layer height (h) would then be proportional to D, as the smaller the layer the less distance under tension to separate the layers. i.e. Adhesion force should be inversely proportional to h. fig. 9(5) and reference (6).
- (b) By applying Deryagin's two term friction law - Chapter 1, equation (4) - to figs 8(2) and 8(3) the same relationship between adhesion force and layer height can be derived.
i.e. $F = \mu_0 (N + N_0)$ where N, the external load is due to the repulsive forces and N_0 due to attractive forces. When $N = 0$; $F_0 = \mu_0 N_0$ and when $F = 0$; $N = -N_0$. As the layer height increases, therefore, N_0 will decrease - i.e. $N_0 \propto 1/h$. Adhesion could also include removal of the absorbed molecules from the surface and any unknown structural changes.

9.8 Light Loads

As was shown section 1.8 there are differences in the interpretation of the action of light loads.

- (a) Bowden and Tabor explain the rise in μ as the film interacting with itself - it has been seen that under a variety of conditions μ is of the order 0.02 - 0.1. There is no mention of variation of parameters as a function of layer height.
- (b) Cameron and Kragelskii both emphasise that there is an intercept on the Force axis and μ is defined as (F/N) . i.e. equation (6) - Chapter (1). Fig 9(6) shows some variations of μ as a function of F_0 . Although this is a plausible explanation it does not really

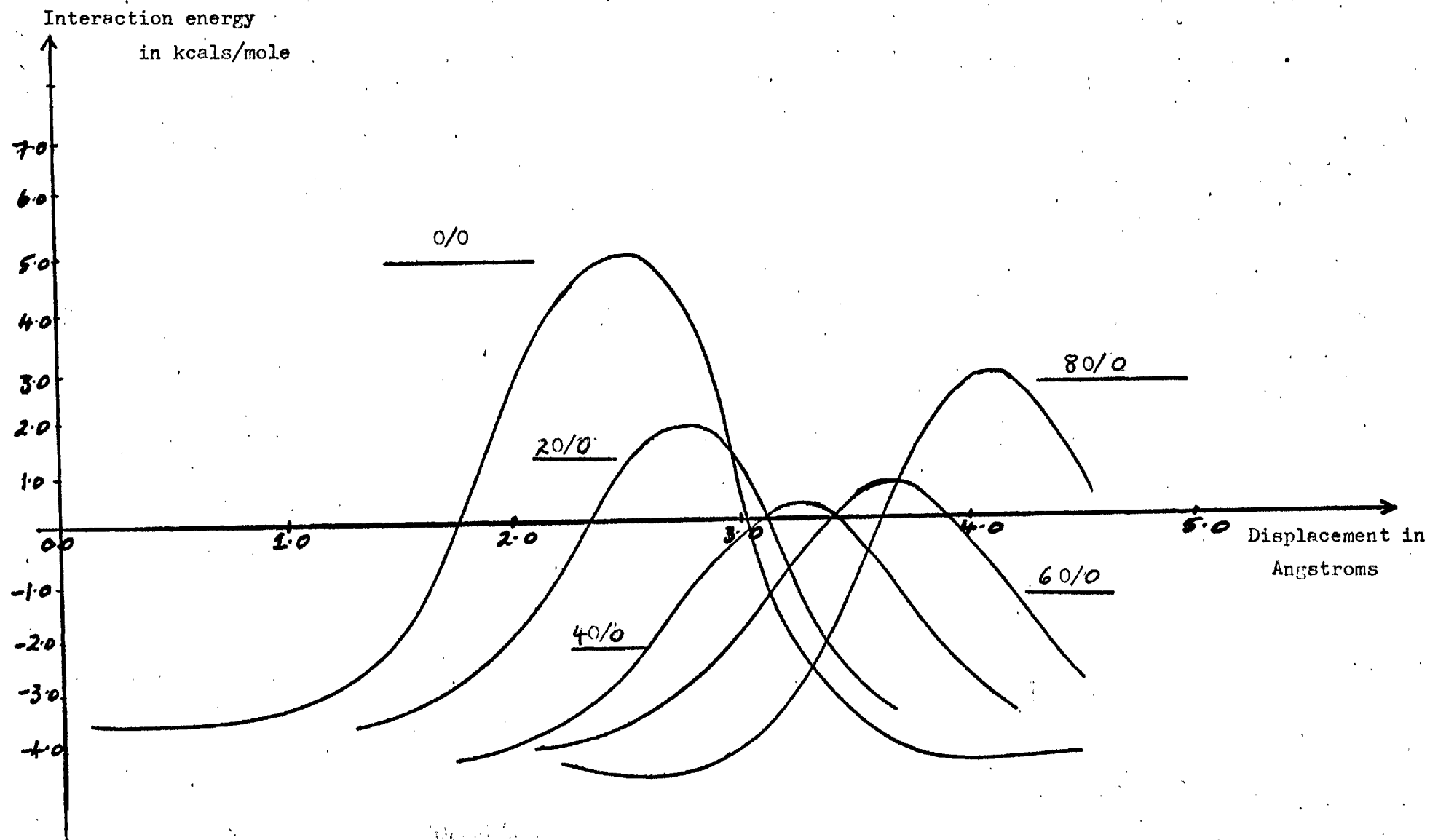


Fig. 9(1) - Effect of rotation (ROT/ROCK) as a function of distance across the X-AXIS; SET (44)

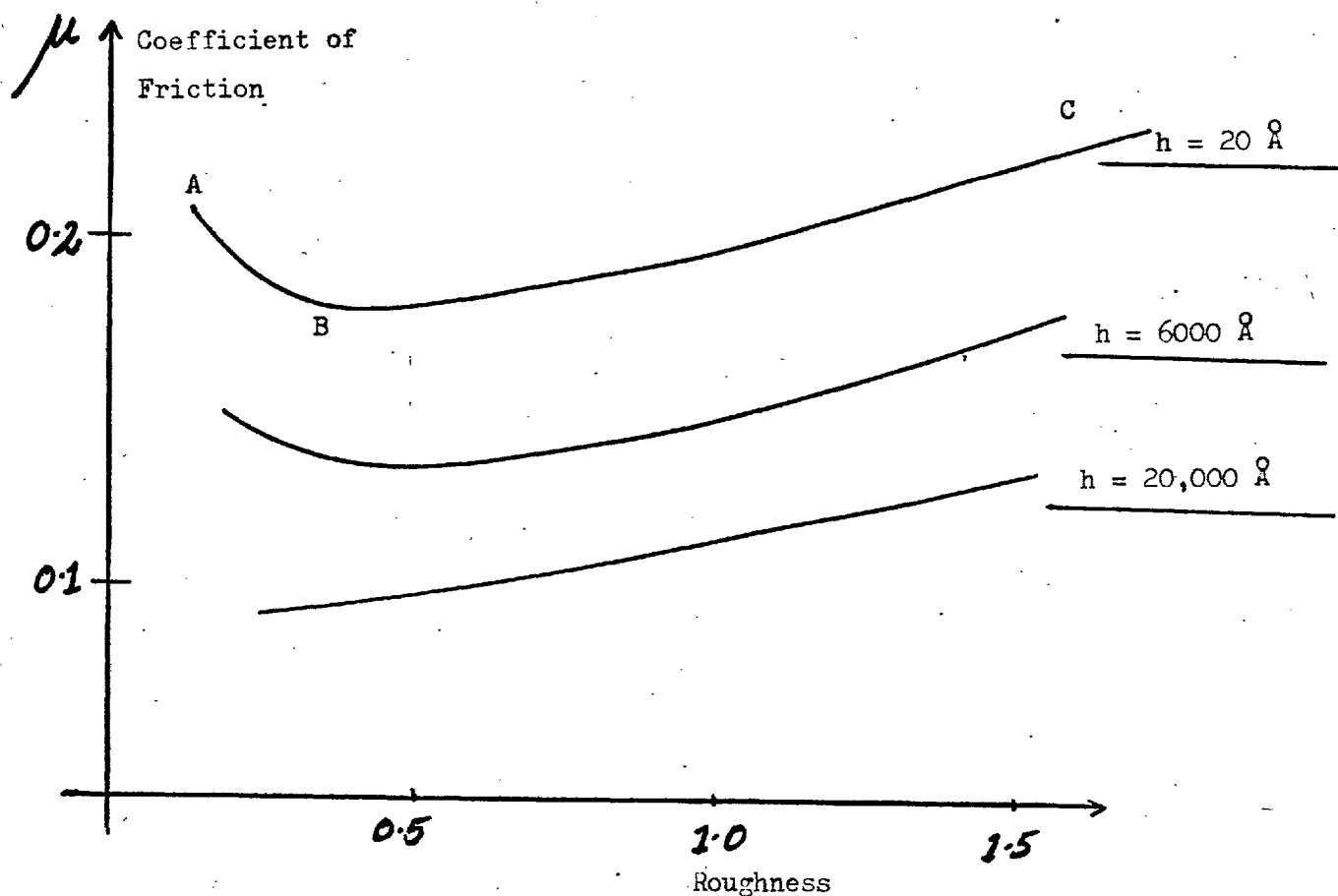


Fig. 9(2) Coefficient of Friction as a function of Roughness and thickness of lubricating film - castor oil.

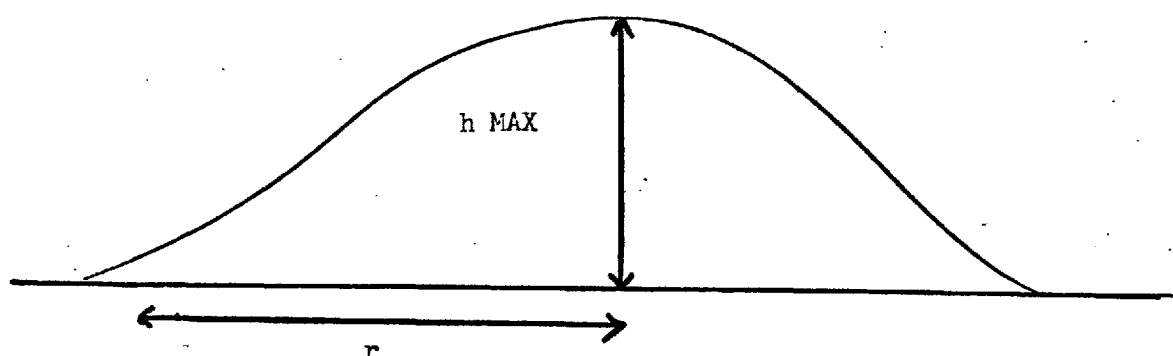
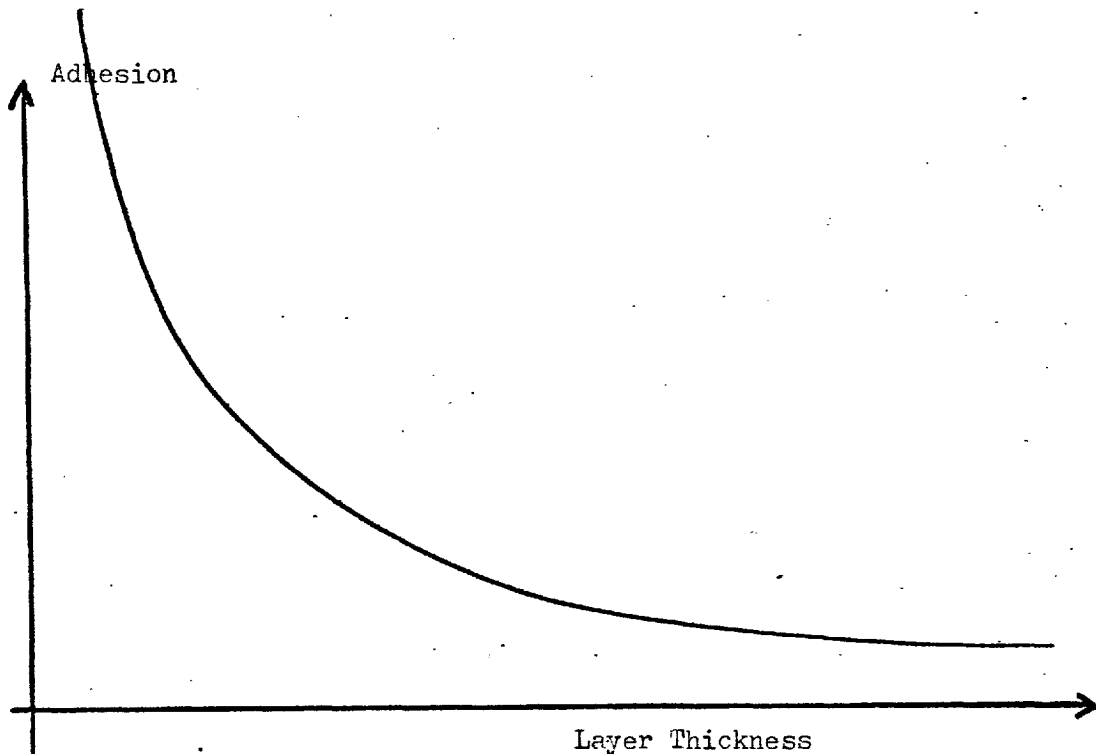
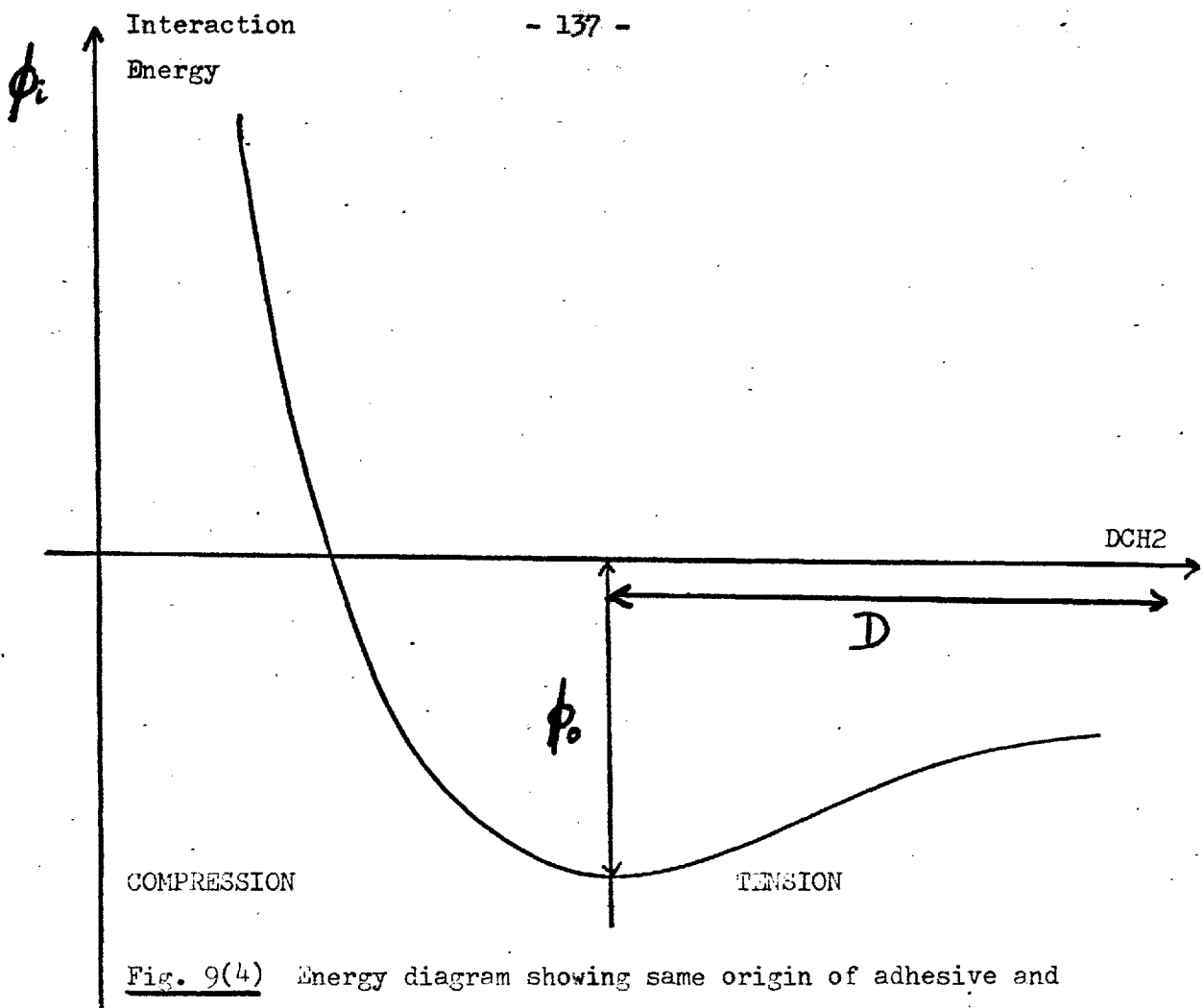
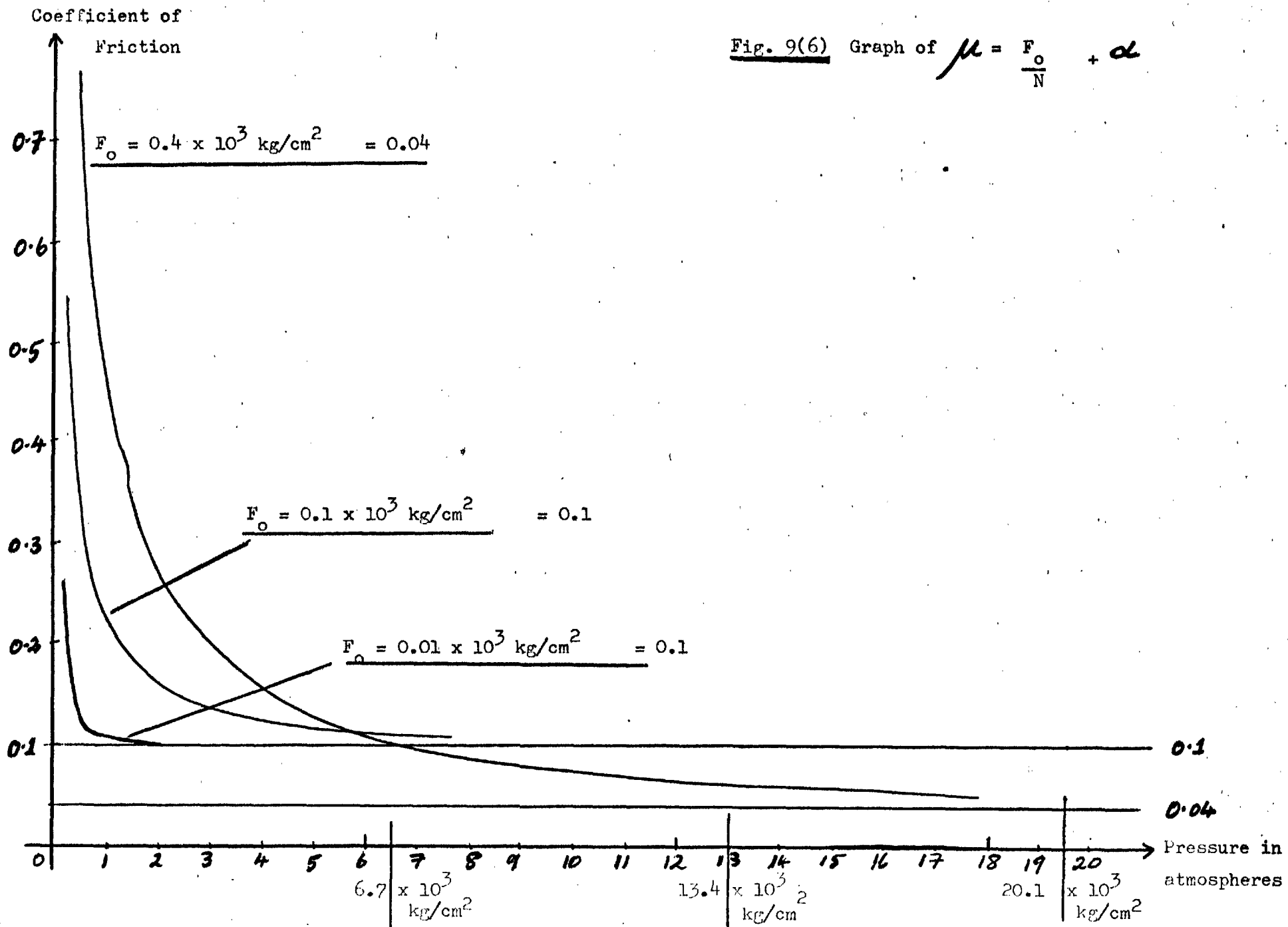


Fig. 9(3) Representation of Surface Roughness





explain what causes the phenomena. Adamson's suggestion that the situation at light loads is similar to figs 1(2) and at normal loads the chains lie flat seems rather dubious, as for large Shift values i.e. chains approaching the horizontal; the interaction energies were very large. Fig. 8(5) does show μ increasing at light loads if a minimum energy profile is taken as a function of rotation. Equation (7) - Chapter 1 - implies that at light loads the area of contact is not proportional to load, this must also help to explain the effect.

9.9 Statistics of Model, Physical and Chemical Adsorption

By considering displacements every 10° across the unit cell a Root Mean Square Value compared to the X-AXIS can be calculated. The same diagrams show the anisotropy of Friction with respect to well defined directions, in particular along the diagonals and Y-AXIS. References (7) and (8) state that physical adsorption of fatty acid molecules on a surface is of the order of 3-10 kcal/mole and Chemical is in excess of this value. Physical films could shift their orientation to the surface so that the shear direction is in effect across the diagonal - this would entail a redistribution of $\pm 15^\circ$ and in consequence must take up a certain amount of work. Chemical films would probably be less inclined to line up along a minimum slip plane.

Fitzgerald (7) states that coefficient of friction will be highest in the direction of closest spacing, which can be seen to occur in the diagrams describing friction parameters as a function of distance and angle. 'Kinetic friction', was assumed to be due to the gliding of one layer relative to the next and 'static' due to the initial displacement which could involve elastic and plastic forces.

9.10 Model and parameters used in the program

- (a) Internal rotations make an appreciable difference in the potential profile - ROCK being the more effective.
- (b) The minimum shift value is 20° to the vertical and internal rotations are not so effective - this system gives the lowest F_0 value. i.e. 60 kg/cm^2
- (c) The Setting Angle was calculated to be 44° .
- (d) Compressions in the a and b directions are of the same order.
- (e) Rotation of the chain are secondary effects.
- (f) A larger lattice size on the X-AXIS would give lower results assuming the same energy dissipation maximum.

9.11 Effect of Solid Phase

Harding (8) assumes the constant A in the force of attraction of two solid surfaces $f_A = A/6\pi R^3$ to be 10^{-12} ergs, see Chapter 1 - equation (8). The force at 20 Å separation is 0.17 /ergs /cm². For very low values of F_0 the solid contribution would be $\approx 10\%$ - at 40 Å separation the contribution is negligible. The question does arise how the solid surface affects the properties of the crystals - i.e. surface deformation, polycrystalline structure, the composition of the surface force and profile.

R E F E R E N C E S

- (1) Bowden F.P. and Tabor D. - Friction & Lubrication (1956) Methuen p. 129.
- (2) Akhmatov A.S. p. 248 - 251
- (3) Godfrey D. - NASA p. 324. See Chapter 1 reference 10
- (4) Wert C.A. and Thomson R.M. - 'Physics of Solids' - McGraw - Hill p. 108 - 113.
- (5) Kragelskii - 'Friction & Wear' - Butterworths (1965) p. 232
- (6) Akhmatov A.S. - p. 273
- (7) Fitzgerald E.R. - 'Particle Waves and Deformation in Crystalline Solids' - Interscience Publication 1966 p. 165 - 166.
- (8) Harding R.D. - Ph.D. Thesis - University of London September 1968.

CHAPTER 10 - CONCLUSION AND FUTURE WORK

10.1 Conclusions

As friction is of a statistical nature it is surprising how many quantitative results can be predicted by use of an idealised system. The main advances achieved in this work may be listed as

- (a) Coefficients of friction were of the right order, i.e. 0.1 $\rightarrow$ 0.03; only one exception was found.
- (b) The magnitude of the frictional force was greater than experimental results by a factor of two to four times, but changes in the assumptions of energy dissipation or dislocations in the crystal structure would diminish the values obtained. Such reductions are to be expected from other published work.
- (c) The basic sensitivity of friction forces with respect to repulsive forces has been shown. By the use of differing potential systems different molecular layer heights can be represented and the relationship between the number of layers and force has been shown. Using this and compression diagrams some experimental results with respect to surface roughness and adhesion can be explained.
- (d) There is no evidence that the rise in coefficient of friction at light load can be explained by lubricant films sliding on themselves but rather this phenomena is more likely to be due to changes in the area of contact with load.
- (e) The anisotropy of calculated frictional forces with respect to direction in ideal crystals has been shown. Minimum shear planes are present and an elementary statistical process can be envisaged by considering a root mean square value over 360° .
- (f) Twisting of the chains has been shown to be a second order effect compared with internal rotations or lifting and the setting angle has been calculated theoretically and shown to agree excellently with practice.

10.2 Improvements of the model and future work

- (a) Similar work could be done for different crystal structures of fatty acids i.e. monoclinic and triclinic systems, to augment work already done.
- (b) Direct substitution of the hydrogen atoms and changing the lattice parameters would lead to systems of more practical nature i.e. fluorine chain compounds and P.T.F.E.
- (c) A sinusoidal internal rotation potential could be developed to give a more accurate portrayal of the minimum energy paths.

- (d) The model could be adapted to incorporate a statistical Fourier representation of metal surfaces.
- (e) A random liquid model of long chain molecules could be investigated for the sake of comparison with crystal structures.

oooooOooooo

APPENDIX A - CHAIN MESHING UNDER COMPRESSION

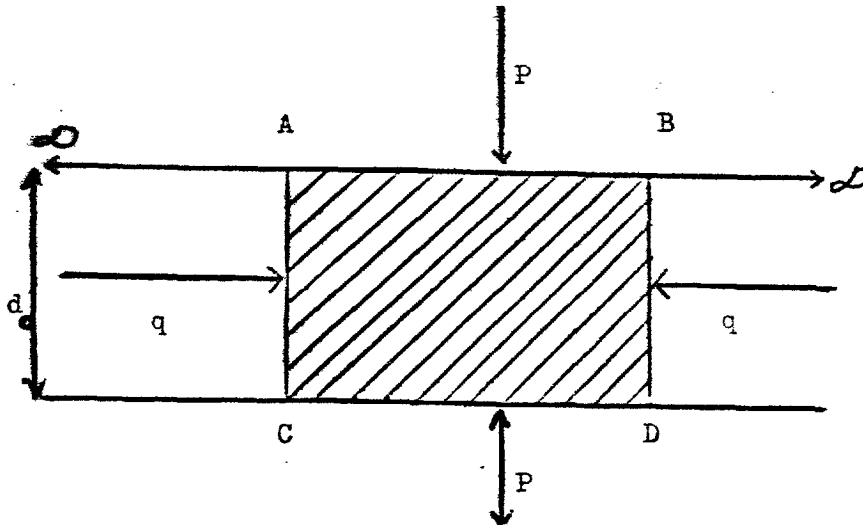
- (a) It has been seen that the chains can resist huge pressure by deformations of a few tenths of Angstroms in the Z direction. i.e. DCH2 values.
- (b) A program was run to reduce DCH2 from 3.09 Å at the equilibrium, to negative values representing the chains in a meshed position.
- (c) When considering values of DCH2 approaching zero, the repulsive forces predominated, but with respect to negative values of DCH2 the attractive forces tended to dominate.

It appears that chain meshing would be an unlikely process unless accompanied by internal rotations to overcome the potential, or by structural changes.

APPENDIX B - INFINITE AND FINITE LAYERS

(see Akhmatov - p. 253)

Consider a boundary layer having a thickness d and extending infinitely in the X and Y direction



Consider ABCD within the layer - apply pressure p and the layer thickness will alter to

$$d = d_0 (1 - \alpha p) \quad \alpha = \frac{1}{E} \quad (E = \text{Young Modulus})$$

But there will be a lateral pressure q in an infinite layer which will prevent lateral extensions - therefore the distance decreased will be less than d i.e. γd

$$d' = d_0 (1 - \alpha' p)$$

? Poisson's ratio?

where $\alpha' < \alpha$ or $E' > E$

Where E' is the modulus for an infinite layer

E is the modulus for a finite layer.

Akhmatov states that elastic compression can be applied to layers of finite dimension if the pressure p does not exceed the resistance to plastic flow in the XY plane i.e. $10^3 - 10^4 \text{ kgm/cm}^2$.

APPENDIX C - MAIN SUBROUTINE OF THE MAIN PROGRAM

The program reproduced (see Chapter 4 for the flow chart), represents rotating a methyl group through 360° (ROT) at a point 2.4 Angstroms on the X-AXIS at a compression value of DCH2 - 2.85 Å (40 tons/sq" - Cameron's loading system). The range of influence of the molecules is 22.2 Å.

The program ran on a CDC 6600 machine, time limit 300 seconds and core - space 30,000 units.

JOB(UMEM070,CM30000,T300,D0)
FUN(S,,,,,11610)
LGO.

SUTCLIFFE

HELP

```

C      MAIN PROGRAM
      PROGRAM HELP (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      INTEGER R,P,Q
      DIMENSION SET(362),F(20),DA(100),BLUE(120),ABA(2)
      COMMON AAX(12),ABX(12),BBX(12),BAX(12),AAXE(12),ABXE(12),BBXE(12),
1BAXE(12),AAXD(12),ABXD(12),BBXD(12),BAXD(12),AAY(15),ABY(15),CAY(1
25),CBY(15),AY(15),CY(15),ABYE(15),Cbye(15),ABYV(15),CBYV(15),AAYD(
315),ABYD(15),CAYD(15),CBYD(15),RX(12),RY(15),RZE1(6),RZE2(6),RZO1(
46),RZO2(6),RZD1(6),CRIT,X1,X2,X3,Y1,Y2,Y3,SCCT,SCHT,SHHT,RP2(1200)
5,RP(1200),SCH2
      READ(5,1000) THETA, HC,ALPHA,A1,A2,BUCK1,BUCK2,BUCKM,C1,C2,C3,H1
1,H2,H3,BUK1,BUK2,BUK3,BUK4,BMUL,BSL,RLJH,BH,BART,HEB,BTLL,AO,CON,E
2RG,CMUL,CSL,CH,UX,UY,CM,CK, (RX(I),I=1,7),(RY(J),J=1,10)
1000 FORMAT (10X,F12.6)
C      *****
C      X-AXIS COMPRESSION
C      SETTING ANGLE FIXED AT 44 DEGREES
      K=46
C
      SET(K-1)=(FLOAT(K-2)*3.14159)/180.0
C
C      CONSTRUCT DISPLACEMENT LOOP
      D=2.4
C
C      CONSTRUCT DISPLACEMENT PARAMENTERS
      MF=1
      ORT=0.0
      F(MF)=ORT*3.14159/180.0
C      COMPRESSION LOOP
C
      DCH2=2.850
C
      D07000 KR=2.362,10
C
C
CD     DEFINE BOND LENGHTS
      DATA (ABA(JI),JI=1,2)/0.4445,0.6940/
      DO 8000 JI=1,2
      AB=ABA(JI)
C
C      -INCREASE Y3 CO-ORD--DECREASE X3 CO-ORD- IE.H3 AVOIDING EACH OTHER
      ROT=FLOAT(KR-2)
C      INTRODUCE COORDINATE AFFECTING ALL H MOLECULES
      HINROT=ROT*3.14159/180.0
C      INTRODUCE TILTING CO-ORD1 (ROCK)------(X3,Y3,Z3)
      TILT=0.0
      ROCK=TILT*3.14159/180.0
      X=AB*COS(SET(K-1))
      Y=AB*SIN(SET(K-1))
      X1=HC*COS(THETA-SET(K-1)-HINROT)
      Y1=HC*SIN(THETA-SET(K-1)-HINROT)
      X2=HC*COS(THETA+SET(K-1)+HINROT)
      Y2=HC*SIN(THETA+SET(K-1)+HINROT)
      X3=HC*SIN(ALPHA+ROCK)*COS(SET(K-1)+HINROT)
      Y3=HC*SIN(ALPHA+ROCK)*SIN(SET(K-1)+HINROT)

```

Z3=HC*COS(ALPHA+ROCK)

DISPLACEMENT IN QUADRANT A

CONSTRUCT X SUMMATION ARRAYS

DO 71 I=1,7,1

AAX(I)=CM+2.0*X+RX(I)-D*COS(F(MF))

ABXE(I)=UX-CK+RX(I)-D*COS(F(MF))

ABXD(I)=-D*COS(F(MF))+UX-CK-2.0*X+RX(I)

ABX(I)=UX-CK+2.0*X+RX(I)-D*COS(F(MF))

BAX(I)=UX-CM-2.0*X+RX(I)+D*COS(F(MF))

BBX(I)=CK-2.0*X+RX(I)+D*COS(F(MF))

AAXE(I)=CM+RX(I)-D*COS(F(MF))

BBXE(I)=CK+RX(I)+D*COS(F(MF))

BAXE(I)=UX-CM+RX(I)+D*COS(F(MF))

AAXD(I)=-D*COS(F(MF))+CM-2.0*X+RX(I)

BAXD(I)=D*COS(F(MF))+UX-CM+2.0*X+RX(I)

BBXD(I)=D*COS(F(MF))+CK+2.0*X+RX(I)

71 CONTINUE

\$ RANGE OF INFLUENCE TEST *****

DO 400 I=1,7,1

IF (AAX(I).GT.22.2) AAX(I)=100.0

IF (ABX(I).GT.22.2) ABX(I)=100.0

IF (BAX(I).GT.22.2) BAX(I)=100.0

IF (BBX(I).GT.22.2) BBX(I)=100.0

IF (AAXE(I).GT.22.2) AAXE(I)=100.0

IF (ABXE(I).GT.22.2) ABXE(I)=100.0

IF (BBXE(I).GT.22.2) BBXE(I)=100.0

IF (BAXE(I).GT.22.2) BAXE(I)=100.0

IF (AAXD(I).GT.22.2) AAXD(I)=100.0

IF (ABXD(I).GT.22.2) ABXD(I)=100.0

IF (BBXD(I).GT.22.2) BBXD(I)=100.0

IF (BAXD(I).GT.22.2) BAXD(I)=100.0

400 CONTINUE

DO 403 I=1,7,1

IF (AAX(I).LT.-22.2) AAX(I)=100.0

IF (ABX(I).LT.-22.2) ABX(I)=100.0

IF (BAX(I).LT.-22.2) BAX(I)=100.0

IF (BBX(I).LT.-22.2) BBX(I)=100.0

IF (AAXE(I).LT.-22.2) AAXE(I)=100.0

IF (ABXE(I).LT.-22.2) ABXE(I)=100.0

IF (BBXE(I).LT.-22.2) BBXE(I)=100.0

IF (BAXE(I).LT.-22.2) BAXE(I)=100.0

IF (AAXD(I).LT.-22.2) AAXD(I)=100.0

IF (ABXD(I).LT.-22.2) ABXD(I)=100.0

IF (BBXD(I).LT.-22.2) BBXD(I)=100.0

IF (BAXD(I).LT.-22.2) BAXD(I)=100.0

403 CONTINUE

CONSTRUCT Y SUMMATION ARRAYS

DO 81 J=1,10,1

AAY(J)=2.0*Y+RY(J)-D*SIN(F(MF))

CAY(J)=UY-2.0*Y+RY(J)+D*SIN(F(MF))

ABY(J)=-D*SIN(F(MF))+RY(J)+UY/2.0

CBYE(J)=D*SIN(F(MF))+RY(J)+UY/2.0-2.0*Y

ABYE(J)=-D*SIN(F(MF))+RY(J)+UY/2.0+2.0*Y

```

ABYD(J)=-D*SIN(F(MF))+RY(J)+UY/2.0
AAYD(J)=-D*SIN(F(MF))+RY(J)-2.0*Y
CAYD(J)=D*SIN(F(MF))+RY(J)+UY+2.0*Y
ABYV(J)=UY/2.0-2.0*Y+RY(J)-D*SIN(F(MF))
CBYV(J)=UY/2.0+2.0*Y+RY(J)+D*SIN(F(MF))
AY(J)=RY(J)-D*SIN(F(MF))
CY(J)=RY(J)+D*SIN(F(MF))
CBY(J)=UY/2.0+RY(J)+D*SIN(F(MF))
CBYD(J)=RY(J)+D*SIN(F(MF))+UY/2.0

```

81 CONTINUE

C ***** RANGE TEST *****

```

DO 401 J=1,10,1
IF (AAY(J).GT.22.2) AAY(J)=100.0
IF (ABY(J).GT.22.2) ABY(J)=100.0
IF (CAY(J).GT.22.2) CAY(J)=100.0
IF (CBY(J).GT.22.2) CBY(J)=100.0
IF (AY(J).GT.22.2) AY(J)=100.0
IF (CY(J).GT.22.2) CY(J)=100.0
IF (ABYE(J).GT.22.2) ABYE(J)=100.0
IF (CBYE(J).GT.22.2) CBYE(J)=100.0
IF (ABYV(J).GT.22.2) ABYV(J)=100.0
IF (CBYV(J).GT.22.2) CBYV(J)=100.0
IF (AAYD(J).GT.22.2) AAYD(J)=100.0
IF (ABYD(J).GT.22.2) ABYD(J)=100.0
IF (CAYD(J).GT.22.2) CAYD(J)=100.0
IF (CBYD(J).GT.22.2) CBYD(J)=100.0

```

401 CONTINUE

```

DO 404 J=1,10,1
IF (AAY(J).LT.-22.2) AAY(J)=100.0
IF (ABY(J).LT.-22.2) ABY(J)=100.0
IF (CAY(J).LT.-22.2) CAY(J)=100.0
IF (CBY(J).LT.-22.2) CBY(J)=100.0
IF (AY(J).LT.-22.2) AY(J)=100.0
IF (CY(J).LT.-22.2) CY(J)=100.0
IF (ABYE(J).LT.-22.2) ABYE(J)=100.0
IF (CBYE(J).LT.-22.2) CBYE(J)=100.0
IF (ABYV(J).LT.-22.2) ABYV(J)=100.0
IF (CBYV(J).LT.-22.2) CBYV(J)=100.0
IF (AAYD(J).LT.-22.2) AAYD(J)=100.0
IF (ABYD(J).LT.-22.2) ABYD(J)=100.0
IF (CAYD(J).LT.-22.2) CAYD(J)=100.0
IF (CBYD(J).LT.-22.2) CBYD(J)=100.0

```

404 CONTINUE

C

C

CONSTRUCTION OF Z ARRAYS

C

```

DO 600 JA=1,6,1
IF (JA.EQ.1) GO TO 601
RZ01(JA)=RZ01(JA-1)+2.54
GO TO 602

```

601 RZ01(JA)=DCH2

GO TO 602

602 CONTINUE

600 CONTINUE

C

C

```

DO 603 JB=1,6,1
IF (JB.EQ.1) GO TO 604
RZ02(JB)=RZ02(JB-1)+2.54

```

GO TO 605
604 RZ02(JB)=(DCH2-Z3)
GO TO 603
605 CONTINUE
603 CONTINUE

CRIT=(DCH2-2.0*Z3)

DO 606 JC=1,6,1
IF(JC.EQ.1) GO TO 607
RZE1(JC)=RZE1(JC-1)+2.54
GO TO 608
607 RZE1(JC)=(DCH2+(2.54/2.0))
GO TO 606
608 CONTINUE
606 CONTINUE

DO 609 JD=1,6,1
IF (JD.EQ.1) GO TO 610
RZE2(JD)=RZE2(JD-1)+2.54
GO TO 611
610 RZE2(JD)=(DCH2+(2.54/2.0)-Z3)
GO TO 609
611 CONTINUE
609 CONTINUE

DO 612 JE=1,5,1
IF(JE.EQ.1) GO TO 614
RZD1(JE)=RZD1(JE-1)+2.54
GO TO 615
614 RZD1(JE)=DCH2+2.54
GO TO 612
615 CONTINUE
612 CONTINUE

IF (AB.EQ.0.6940) GO TO 902

WRITE (6,5)
5 FORMAT (1H1, //20X, 56H COMPRESSION READINGS FOR SETTINGS ANGLE AT
144 DEGREES /20X, 56H-----
2-----/)

WRITE(6,100) DCH2
100 FORMAT (40X, 8H DCH2 = ,F7.4/40X, 10H-----/40X, 10H-----/)
WRITE (6,9000) D
9000 FORMAT (20X, 5H D = ,F5.3/)

WRITE (6,306) K,ROT,TILT,CRIT,DCH2,ORT
306 FORMAT (5X,6HSET = ,I3,6HROT = ,F8.4,7HTILT = ,F8.4,7HCRIT = ,F9.5
1,7HDCH2 = ,F8.4,6HORT = ,F8.4/)
CALL REPULSIVE SUBROUTINE
CALL RHH

WRITE (6,300)
300 FORMAT (20X, 67H LIST OF SMALLEST DISTANCES AND CORRESPONDING REPUL
SIVE POTENTIALS)

C**** SUM UP RELEVANT DISTANCES ***

C

SUM1=0.0

SUM2=0.0

SUM3=0.0

SUM4=0.0

SUM5=0.0

SUM6=0.0

SUM7=0.0

SUM9=0.0

DO 7001 KA=1.1152,1

IF (RP2(KA).EQ.4.0) GO TO 7001

C

C*** BUCK-EXP POTENTIALS ***

C

C BARTON KCALS/MOLE

C

E11=BUK1*EXP(-BART*RP2(KA)/A0)*CON*2.0

SUM1=SUM1+E11

C HENDERSON KCALS/MOLE

C

E12=BUK2*EXP(-BART*RP2(KA)/A0)*CON*2.0

SUM2=SUM2+E12

C HENDERSON-BARTELL KCALS/MOLE

C

E13=BUK3*EXP(-HEB*RP2(KA)/A0)*CON*2.0

SUM3=SUM3+E13

C BARTELL S/MOLE

C

E14=BUK4*EXP(-BTLL*RP2(KA)/A0)*CON*2.0

SUM4=SUM4+E14

C MULLURS POT

C

E15=BMUL*EXP(-CMUL*RP2(KA)/A0)*CON*2.0

SUM5=SUM5+E15

C SLATERS HELIUM MODEL

C

E16=BSL*EXP(-CSL*RP2(KA)/A0)*ERG*2.0

SUM6=SUM6+E16

C 6-12 POT

C

E17=RLJH*2.0/(RP2(KA)**12)

SUM7=SUM7+E17

E19=(2.0*CON*0.818*RP2(KA)**(5/2)*EXP(-2.0*RP2(KA)/A0))/(A0**(5/2)

1)

SUM9=SUM9+E19

IF (RP2(KA).LT.1.8) GO TO 301

GO TO 7001

301 CONTINUE

RP2D=RP2(KA)

WRITE (6,302) KA,RP2D,E11,E12,E13,E14,E15,E16,E17

302 FORMAT (1X,I4,8(E13.6))

7001 CONTINUE

SU1=0.0

SU2=0.0

SU3=0.0

SU4=0.0

SU5=0.0

SU6=0.0

SU7=0.0

SU9=0.0

DO 7002 KB=1.1152.1

IF (RP(KB).EQ.4.0) GO TO 7002

C BARTON KCALS/MOLE

E21=BUK1*EXP(-BART*RP(KB)/A0)*CON

SU1=SU1+E21

C HENDERSON KCALS/MOLE

E22=BUK2*EXP(-BART*RP(KB)/A0)*CON

SU2=SU2+E22

C HENDERSON-BARTELL KCALS/MOLE

E23=BUK3*EXP(-HEB*RP(KB)/A0)*CON

SU3=SU3+E23

C BARTELL S/MOLE

E24=BUK4*EXP(-BTLL*RP(KB)/A0)*CON

SU4=SU4+E24

C MULLURS POT -

E25=BMUL*EXP(-CMUL*RP(KB)/A0)*CON

SU5=SU5+E25

C SLATERS HEL+UM MODEL

E26=BSL*EXP(-CSL*RP(KB)/A0)*ERG

SU6=SU6+E26

C 6-12 POT -

E27=RLJH/(RP(KB)**12)

SU7=SU7+E27

C HIRCHFELDER

E29=(CON*0.818*RP(KB)**(5/2)*EXP(-2.0*RP(KB)/A0))/(A0**(5/2))

SU9=SU9+E29

IF (RP(KB).LT.1.8) GO TO 303

GO TO 7002

303 CONTINUE

RPD=RP(KB)

WRITE (6,304) KB,RPD,E21,E22,E23,E24,E25,E26,E27

304 FORMAT (10X,14.8(E13.6))

7002 CONTINUE

C

C SUM TOTAL OF REPULSIVE POTS KCALS/MOLE

C

R1=SUM1+SU1

R2=SUM2+SU2

R4=SUM4+SU4

R5=SUM5+SU5

R6=SUM6+SU6

R7=SUM7+SU7

R9=SUM9+SU9

C

C CALL ATTRACTIVE DISTANCES SUBROUTINES

C

CALL CC

CALL CHD

CALL HH

ECC1=A1*SCCT*ERG

ECH1=A2*SCHT*ERG

EHH1=BUK2*CON*SHHT*(A0**6)

EATR=ECC1+ECH1+EHH1

GO TO 8000

902 CONTINUE

CALL CH2

GO TO 8000
8000 CONTINUE

C DATA ECH2/595.0/
EAT2=SCCH2*ECH2
ESKB2=R1-EAT2
ESKBT2=R4-EAT2
ESKM2=R5-EAT2
ESKSL2=R6-EAT2
ELJ2=R7-EAT2
ESKH2=R9-EAT2

C C SUM ATTRACTIVE POT AND REP POT TO OBTAIN INTERACTION ENERGY

C
ESKB=SUM1+SU1-(A1*SCCT+A2*SCHT)*ERG-BUCK2*CON*SHHT*(A0**6)
ESKH=SUM2+SU2-(A1*SCCT+A2*SCHT)*ERG-BUCK2*CON*SHHT*(A0**6)
ESKHBT=SUM3+SU3-(A1*SCCT+A2*SCHT)*ERG-BUCK2*CON*SHHT*(A0**6)
ESKBT=SUM4+SU4-(A1*SCCT+A2*SCHT)*ERG-BUCK2*CON*SHHT*(A0**6)
ESKM=SUM5+SU5-(A1*SCCT+A2*SCHT)*ERG-BUCK2*CON*SHHT*(A0**6)
ESKSL=SUM6+SU6-(A1*SCCT+A2*SCHT)*ERG-BUCK2*CON*SHHT*(A0**6)
ELJ=SUM7+SU7-(C1*SCCT+C2*SCHT+C3*SHHT)
ESKHCH=R9-(A1*SCCT+A2*SCHT)*ERG-BUCK2*CON*SHHT*(A0**6)

C WRITE OUTPUT

WRITE (6,500)

500 FORMAT (10X,24H SUM OF DISTANCES CLASSES)

WRITE (6,800) SCCT,SCHT,SHHT

800 FORMAT (6X,8H SCCT = ,E13.6,8H SCHT = ,E13.6,8H SHHT = ,E13.6/)

WRITE (6,505)

505 FORMAT (25X,20H REPULSIVE POTENTIALS)

WRITE (6,501)

501 FORMAT (12X,6HBARTON,4X,7HBARTELL,3X,6HSLATER,2X,9HLEN-JONES,2X,11
1HHIRCHFELDER)

WRITE (6,801) R1,R4,R6,R7,R9

801 FORMAT (10X,5E10.4/)

WRITE (6,504)

504 FORMAT (50X,26H TOTAL ATTRACTIVE POTENTIAL)

WRITE (6,804) EATR,EAT2

804 FORMAT (50X,8H EATR = ,E13.6,8H EAT2 = ,E13.6/)

WRITE (6,502)

502 FORMAT (30X,21H ATTRACTION POTENTIALS)

WRITE (6,802) ECC1,ECH1,EHH1

802 FORMAT (6X,8H ECC1 = ,E13.6,8H ECH1 = ,E13.6,8H EHH1 = ,E13.6)

WRITE (6,503)

503 FORMAT (50X,19H INTERACTION ENERGYS/13X,4HESKB,6X,4HESKH,5X,6HESKHB
2T,4X,5HESKBT,6X,4HESKM,6X,5HESKSL,5X,3HELJ,5X,11HHIRCHFELDER)

WRITE (6,803) ESKB,ESKH,ESKHBT,ESKBT,ESKM,ESKSL,ELJ,ESKHCH

803 FORMAT (10X,8E10.4/)

WRITE (6,807)

807 FORMAT (40X,39H SCATTERING CENTERS-INTERACTION ENERGIES/22X,5HESKB2
1,8X,6HESKBT2,8X,5HESKM2,8X,6HESKSL2,8X,4HELJ2,8X,5HESKH2)

WRITE (6,806) ESKB2,ESKBT2,ESKM2,ESKSL2,ELJ2,ESKH2

806 FORMAT (20X,6E13.6)

7000 CONTINUE

STOP

END